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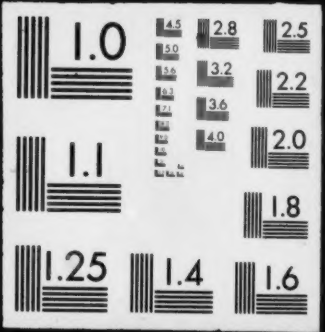
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Texas Univ. at Austin

Prepared for

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16. ABSTRACT

Land treatment represents one of the alternatives for management of municipal and industrial wastes. Hazardous waste land treatment systems are intended to degrade, immobilize and/or transform applied wastes into innocuous constituents and to avoid bioaccumulation of hazardous constituents in the food chain. A specialty conference held in Austin, Texas, in April 1985 represented a comprehensive attempt to critically examine the current state-of-knowledge with regard to land treatment of hazardous wastes. This volume contains peer-reviewed papers presented at this conference. Emphasis was placed not on the type of waste that may be applied but on the transformations and the environmental impact which may occur when land treatment is used for the management of industrial wastes.

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PREFACE

The basic needs of man include food, fiber, fuel, and shelter. In earlier times man could and did cycle available resources. The basic cycle was one of the land furnishing fuel, fiber, shelter, and food to the producer and other consumers. A portion of the residues from harvesting and processing were used directly, and the remainder, as well as human and animal wastes, was returned to the land to enrich the soil and enhance crop production. This approach had the benefit of optimum utilization of residues and wastes but resulted in a low level of productivity.

Subsequently, inexpensive fossil fuel energy, inorganic fertilizers, greater mechanization, and use of man-made organic chemicals increased agricultural and industrial productivity and raised the standard of living. However, the production-land link was broken. Residues and wastes were no longer as well utilized and recycled, human and industrial waste production increased, and linear waste production, treatment, and disposal, rather than circular waste utilization approaches became predominant.

Since about 1972, however, there has been a resurgence of interest in the use of land as a waste management alternative for municipal and industrial wastes. Experience has shown that land treatment of wastes can be a practical, reliable, and cost-effective method of treatment and disposal. Compared to other disposal options, properly designed and managed land treatment systems carry low short- and long-term liabilities.

Of the three locations for the ultimate disposal of wastes—surface waters, atmosphere, and land—the land represents not only an appropriate location for the treatment and disposal of wastes, but also an opportunity to manage wastes with minimum adverse environmental impacts. The objectives of land treatment are to degrade, immobilize and/or transform wastes into nondetrimental constituents and to avoid the bioaccumulation of adverse constituents in the food chain.

In the United States, there are over 200 industrial waste land treatment sites and a greater number of land treatment sites for municipal wastewater and sludges. Of the industrial land treatment facilities, about half are used for wastes generated by the petroleum refining industry. There are, however, continuing concerns about the contamination of groundwater and other components of the environment by the land disposal of wastes, particularly hazardous wastes. A manifestation of these concerns has been the prohibition of the land disposal of specified wastes. As an example, "The Hazardous and Solid Waste Amendments of 1984," state that the land disposal of specific wastes is prohibited unless the Environmental Protection Agency (EPA) determines that the prohibition of one or more methods of land disposal is not required to protect human health and environment for as long as the waste remains hazardous. Land treatment is one of the designated land disposal methods that is to be evaluated for its impact on human health and the environment.

This volume represents a comprehensive attempt to critically examine the state of knowledge with regard to land treatment. The papers included in these proceedings are an assessment of land treatment as a waste management alternative for industrial wastes and particularly for hazardous wastes. The papers

1. describe the transport and fate of organic and inorganic compounds applied to land treatment systems;
2. describe the degradation, immobilization, volatilization and bioaccumulation of organic and inorganic constituents that occur when wastes are land treated;
3. indicate monitoring approaches that are appropriate for unsaturated and saturated soil;
4. summarize current research and studies; and
5. present case studies of existing land treatment systems.

The emphasis of this volume is not on the type of waste that may be applied but on the transformations and on the environmental impact that occur when land treatment is used for the treatment and disposal of industrial wastes. All of the authors are recognized experts on the noted topics.

The following papers were presented orally at the conference but not as a technical paper for inclusion in this volume: State Regulations and Guidelines Related to the Land Treatment of Industrial Wastes, C. Smith, Texas Department of Water Resources, Austin, Texas; Land Disposal Prohibition of Hazardous Wastes: A Status Report, A. S. Corson and S. Bromm, Office of Solid Wastes, Environmental Protection Agency, Washington, D.C.; Guidelines for Ground Water Protection, J.H. Lehr, Water Well Association, Worthington, Ohio; and current EPA Regulations for Hazardous Waste Land Treatment, J.Perry, Environmental Protection Agency, Washington, D.C.

The success of the conference at which these papers originated was due in equal measure to the quality of the presentations, the interest and discussion of the participants, and the skill of the moderators. Those who attended the conference were state, regional, and federal regulatory personnel, individuals responsible for industrial process control and waste treatment and management, consulting engineers, and individuals from universities and nonprofit organizations. Approximately 60% of the attendees were from industry, 30% were from government agencies, and the remainder from universities and private organizations.

The knowledge related to using land as a waste management alternative is changing rapidly. However, it is expected that many of the papers in this volume will stand the test of time and will provide insight and baseline information on the proper use of this important waste management alternative.

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The papers in this volume resulted from the national specialty conference, "Land Treatment: A Hazardous Waste Management Alternative" which was held in Austin, Texas in April 1985. The primary sponsors of the conference were: (a) the Environmental Engineering Program, Civil Engineering Department and the Center for Research in Water Resources, College of Engineering, The University of Texas at Austin and (b) the United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

Cooperators in sponsoring the conference were the American Petroleum Institute, Washington, D.C., the Southern Pressure Treaters Association, Shreveport, Louisiana, and the Texas Department of Water Resources, Austin, Texas. We appreciate the assistance of individuals from these and other organizations who served as moderators of specific sessions: Earnest F. Gloyna, David Reed, J. Eldon Rucker, Norman B. Jones, and Joseph F. Malina, Jr.

This conference was the twelfth in a series sponsored by the College of Engineering and the Center for Research in Water Resources, The University of Texas at Austin on varying water resources and environmental topics. Financial support for this conference was provided in part by the Environmental Protection Agency, cooperative agreement CR-812131-01. Mr. John E. Matthews, the project officer for the cooperative agreement provided considerable assistance in the organization of the conference and in identifying and acquiring speakers. The financial support of EPA and the assistance of Mr. Matthews are gratefully acknowledged.

The papers in this volume have been peer reviewed prior to publication. This review and the cosponsorship by the U.S. Environmental Protection Agency does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency or any of the other sponsors, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors.

OPENING REMARKS AND WELCOME

Gerhard J. Fonken
Vice President for Academic Affairs and Research
The University of Texas at Austin
Austin, Texas

On behalf of The University of Texas at Austin, let me welcome you to this very important national conference. We are pleased to have the U.S. Environmental Protection Agency, the American Petroleum Institute, the Southern Pressure Treaters Association, and the Texas Department of Water Resources cosponsor this conference with us. The University of Texas at Austin has had a long standing and mutually satisfactory professional and research relationship with industry and government agencies, and we are delighted to continue such relationships in this manner.

About twenty years ago president Lyndon B. Johnson made some observations that have a bearing on this conference. He noted:

> We live with history. It tells us of a hundred proud civilizations that have decayed through careless neglect of the nature that fed them. . . . We live with the certain future of multiplying populations whose demands on the resources of nature will equal their numbers.

His remarks were addressed to the broad issues and problems of the environment in which we live. This environment must not only feed and house growing populations but must cope with the increasingly complex waste products of high density populations and highly technological societies.

The problems of hazardous waste management are real and pressing. No one is immune to them—although some prefer not to talk about them. The search for scientific and technological solutions to these problems is not enough, because what may be technologically sound may not be politically acceptable, and what may be scientifically logical may stir great emotional opposition. At times no solution is acceptable and as a consequence the problems grow in magnitude and complexity. Therein lies the challenge posed by the issues of waste management.

You will be discussing these and other challenges in the next few days. The conference program is packed with pertinent presentations to be made by recognized experts, including several from our own University. I am sure that the information will be valuable and the discussion stimulating.

In closing, let me reiterate my welcome to Austin and to the conference and let me wish you success as you discuss these critically important issues.

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HEALTH RISK ASSESSMENTS FOR HAZARDOUS WASTE

Robert Bernstein, M.D., F.A.C.P.
Commissioner of Health
Texas Department of Health
Austin, Texas

In the Book of Deuteronomy it is recorded that God instructed the Israelites to go outside their camp to bury their wastes. Early historic and prehistoric man moved on to another site when his habitat became unlivable. The middens we dig through today to discover what life was like in those years were trash heaps at the time.

In Stephen F. Austin's colony at San Felipe, the council appointed a health official whose duty was to see that dead animals and other wastes were taken out of the city for disposal.

Fifty years ago we began to dignify our waste burial sites by calling them "sanitary landfills." By today's standards, these were dumps under the guise of sanitary landfills. They did, however, serve the purpose of providing organized places where community waste could be disposed of without causing a good deal of harm. It was certainly better than having garbage in the streets and alleys of our cities, and it did reclaim land. La Guardia airport is built on a peninsula of garbage. It may be shocking to know that a part of what is now Zilker Park in Austin was a garbage dump.

Today, we can't go outside our camp to bury our waste—if we do, we're in the camp of another. We can't move on after we've fouled our own habitat. And, the safe disposal practices of yesteryear are no longer adequate for the disposal of the by-products of a modern society. We live in a global ecosystem that is finite. An intimate relationship exists between man and his environment. We may alter our environment, but we must weigh the benefits against the effects.

Advances in technology have given us prosperity, and this prosperity has brought risks not even dreamed of 100 years ago. The automobile, a product of this century, has dramatically changed our society. It has also increased our risks. One of every 3,500 Texans will die this year from an automobile accident. This is a simple illustration of the risk and benefit principle at work in our lives. When we place ourselves in a car to go someplace, we make a risk-benefit decision.

This risk-benefit order touches on nearly every aspect of our lives. Love Canal—a complex story involving several layers of bureaucrats, scientists, industry, news media, environmentalists and blameless victims—brought attention to the indiscriminate disposal of industry by-products. The Washington Post recently reported there are more than 60,000 chemicals in commercial use in the

United States, and we produce 1,000 new chemicals each year. According to the article, there are more than 35,000 pesticides, 8,600 food additives, and 3,400 cosmetic ingredients. The same article reported that the annual production of synthetic organic chemicals has increased thirty-five times since World War II.(1)

William D. Ruckelshaus, in an address to the National Academy of Science, said, "we must assume that life now takes place in a mine field of risks from hundreds, perhaps thousands, of substances. . . . No more can we tell the public: 'you are home free with an adequate margin of safety.' "(2)

The risks we face in today's chemical maze were suddenly manifested when more than 2,000 people in Bhopal, India, died from a gas leak at a pesticide plant. This may have been a preventable accident, but nevertheless it focused our attention for a brief time on the risks of chemicals that have become an integral part of our lives. We bemoan the death and injuries from the Bhopal incident and seek answers to how such an occurrence can be prevented elsewhere. In our search for answers, let's not lose sight of the benefits that can be attributed to such plants. How many thousands have been saved from starvation by the application of pesticides produced by the Bhopal plant? It would be mindless not to try to reduce the risks that may be inherent in order to enjoy the benefits of modern science. Dean Gloyna, sometime ago in response to a department solid waste publication, very pointedly said, "there can be no zero risks." And there can be no disagreement with his statement. I think we can agree, however, that we should reduce our risks.

Often we can do very simple things. For instance we can reduce our risk of being killed in an automobile accident by 50% if we use seat belts. And also, let's not lose sight of the fact that the overwhelming risks of cancer are not from man-made carcinogens but from man's abuse of naturally-occurring substances. I need only cite the incidences of cancer from use of tobacco to make my point.

In their book, *The Causes of Cancer*, two medical research scientists, Doll and Peto, reported that only 2% of all cancers resulted from pollution while 30% occurred from tobacco use. Less than 1% were attributable to food additives, but 35% were diet-connected.(3)

Determining the risks associated with chemicals and their waste products is a very complex matter. However, this should not deter us from our pursuit of identifying and reducing those risks.

The federal law we have come to know as RCRA was passed by the 94th Congress with the high purpose of protecting human health and the environment. The law defines waste as being hazardous if it poses a present or potential substantial hazard to human health. The law directed EPA to develop standards for the management of hazardous waste to protect human health and the environment.

I emphasize the provision in the law on protecting human health. I also emphasize that until the passage in November of the reauthorization bill amending RCRA, there was little if any provision in the law or EPA rules on identifying health risks and what to do about them.

At a recent hearing before EPA, a man, whose farm is in the vicinity of a hazardous waste disposal site, related that in the permit application there was a detailed description of the land use, the number of cattle in the fields adjacent to the site, but not one mention of his family residing on the adjacent farm.

Under the RCRA amendments of 1984, owners of hazardous waste land disposal sites are required to report the exposure potential to humans. There are also provisions for health risks assessments associated with such exposures.

The state Legislature, in passing the Solid Waste Disposal Act, provided that the Texas Department of Health (TDH) would be consulted on the health aspects of managing solid waste in Texas. One way in which this provision of the law is implemented is through the TDH's review of industrial solid waste facility permit applications submitted to the Texas Department of Water Resources. This gives us an opportunity to evaluate and assess the health aspects of all facility operations.

Even with the authority and requirements of state and federal laws, we are stymied in making health assessments of hazardous waste operations because of lack of funding. The 68th Texas Legislature denied our request for funds to provide an environmental epidemiological capability, and it appears that a similar request before the 69th Legislature will not be approved. EPA has also denied requests to fund this effort under RCRA.

A recent study of risk assessment in the federal government conducted by a committee of the National Research Council defines risk assessment as the characterization of the potential adverse health effects of human exposures to environmental hazards. The committee describes risk assessment as a four-step process: (a) identifying the toxic properties of the waste; (b) making a dose-response assessment; (c) measuring or predicting the magnitude of human exposure to environmental agents; and (d) estimating the incidence of health effects under various conditions of human exposure.(4)

In these steps, logical and scientific processes exist. Imprecise and uncertain judgements can also be found in these steps. Epidemiological studies are the most precise method of determining the relationship between exposure and disease. Within these studies data is often unavailable; the number of persons exposed is small, the time between exposure and resulting health effects is long, and exposures are varied. In the absence of epidemiological investigations, we must use experimentally-derived relationships of dose and risk. This requires extrapolation of toxic effects on test animals to humans and the prediction of low-dose risks from high-dose and high-risk data.

One important feature of using predictive models is that they almost always incorporate worst-case assumptions. So we can be reasonably assured that if predicted health risks are low, they will in fact be low. However, if we use predicted risks for regulatory control, we may be far too stringent in our decisions. For a regulatory agenda, we should be more precise in our determinations. The recent EDB scare is an example of proposing the use of imprecise information in establishing regulatory control.

This is a very important issue on government control. We can assess risks—albeit imprecisely—and we can analyze benefits that may result from use of substances that pose potential harm. However, I agree with Russell Train, the first EPA Administrator, when he said, "it has become increasingly clear that risks cannot be eliminated completely without unacceptable social and economic consequence."(5) In the absence of clear statutory direction, application of the risk-benefit analysis for regulatory control must be done with great care and remain free of political bias.

I have now reached a point in my discussion where toxic waste managers are involved. In the department's process of evaluating health risks, a general application of the four-step process is used. Potential exposure from air emissions and groundwater and surface water are the main concerns. However, we do not neglect the potential of exposure by personal contact resulting from lax security and poor worker training. Also, an important element of risk assessment is determining the population at risk. It goes without saying that a site in the Houston metroplex offers a greater exposure potential than a site in Loving County. So that I don't get bombarded by the 91 citizens in Loving County, let me say that I'm not by any means suggesting we ship Houston waste to them. My point is that siting is a major factor in reducing health risks. Environmental controls are likewise of utmost importance in reducing human exposure to the toxic effects of our waste products. In these two areas, waste managers play a major role.

Attendance at conferences such as this one is evidence of interest and desire to manage waste in a manner that will reduce the potential for human exposure and thereby reduce health risks. Treatment of hazardous or nonhazardous waste offers a preferable alternative to disposal. Land treatment is an economical and environmentally sound means of managing many residual materials from industrial, commercial, and community operations.

I am pleased to note that one session of the conference deals with the land application of municipal wastewater treatment plant sludges. TDH, as the regulator of these wastes, instituted rules last August that encourage the beneficial use of sludges through land application. Since that time, we have registered about 50 sites covering almost 20,000 acres and the application of about 80,000 tons of sludge annually. Although this figure is about 20% of the waste produced by sewage treatment plants in the state, a very small percentage of the total waste is processed by land treatment—not nearly the amount that could be safely treated by this means.

I encourage further studies of the types of waste that can be safely and economically treated by using the microbial capacity of the soils and their ability to absorb and inactivate waste components. In this pursuit, the health implications that may arise from an indiscriminant or improper use of this medium to reduce our waste products must be considered.

The agenda for this conference reveals a comprehensive coverage of the topic and the conference leaders are to be commended for assembling an excellent array of experts to guide you through some very sophisticated and highly technical studies.

ENDNOTES

1. Cass Peterson, "Risk-Benefit Analysis is Key Tool in U.S. Regulation of Chemicals," The Washington Post, 3 Jan. 1985, p. A6.

2. Ibid.

3. Sir Richard Doll and Richard Peto, The Causes of Cancer: Quantitative Estimates of Avoidable Risks of Cancer in the United States (New York: Oxford University Press, 1981), p. 1256.

4. National Research Council, Risks Assessment in the Federal Government: Managing the Process (Washington, D.C.: National Academy Press, 1983), p.3.

5. Federal Register 41, No. 102, 25 May 1976, p. 21402.

LAND TREATMENT
AS A WASTE MANAGEMENT TECHNOLOGY

AN OVERVIEW

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INTRODUCTION

Land treatment is a waste management technology that has received increasing attention in the past several decades. This interest has resulted from: (a) a recognition that this technology can successfully treat municipal wastewaters and sludges as well as many industrial wastes and (b) the desire to utilize waste management technologies that are less energy intensive and less costly.

Land treatment is a managed treatment and ultimate disposal technology that involves the controlled application of a residue or waste onto or into the soil followed by continued monitoring and management. The wastes are applied to the surface of the soil or incorporated in the surface soils by direct injection or by plowing or tilling. The objectives of land treatment are: (a) the biological degradation of organic waste constituents, (b) the immobilization of inorganic waste constituents, and (c) to avoid the bioaccumulation of waste constituents that may be detrimental to human health and the environment.

Land treatment is less frequently being considered as a black box in which a waste is incorporated in the surface soils and there is hope that what moves through the soil is not detrimental to the groundwater, the terrestrial ecosystem, or to human health. That hope, that incomplete knowledge, has now been replaced with better knowledge and experience so that the reactions, the transformations, the transport, and the fate of applied constituents are better understood and able to be predicted. The existing knowledge concerning the use of this technology has resulted from research and field experience and is based on scientific and engineering principles. As a result, land treatment is a technology that can be protective of human health and the environment.

Information about the performance of land treatment systems as well as guidelines for design and operation are available in many manuals and books (1–6). This technology has been used widely for municipal wastewaters, for municipal and industrial sludges, and for specific industrial wastes such as from the food processing industry and from the petroleum industry. However, land treatment should not be thought of as only useful for such wastes. A broader array of wastes from virtually every industrial category (except radioactive materials) can be considered for land treatment. In addition, the technology of land treatment can be considered for restoration of contaminated soils, for in-situ treatment and for spills. The potential applications of land treatment are summarized in Table 1. The applicable wastes include liquids, semisolids and solids as well as those that have a degree of hazard ranging from zero to large.

TABLE 1. Land treatment technology can be applied to many wastes and situations.

- Municipal wastewaters
- Municipal sludges
- Industrial wastewaters
- Industrial sludges
- Hazardous wastes
- Contaminates soils
- Spills
- In-situ treatment

With certain wastes the total land requirement to treat these wastes in an environmentally sound manner may be very large and land treatment may not be an economic waste management alternative. The decision to use or not use a land treatment technology for the treatment and disposal of a waste is an economic as well as a technical decision. In-depth waste and site specific investigations are used to identify the technical and economic feasibility of this technology. The design and operational requirements for a land treatment site focus on maximizing the treatment of the applied waste constituents by degradation, transformation, and immobilization processes within the treatment zone and on minimizing the escape of such constituents to the groundwater, surface water, or to the atmosphere.

Land treatment frequently is perceived as useful only for wastes that have agronomic benefit and where crops are to be grown. Crops need not be grown at each land treatment site, especially where industrial wastes are applied. Successful land treatment focuses on maintaining the long term viability of land treatment sites for future use rather than on the short term agronomic status of a site.

The environmental objective of a land treatment system is to: (a) use the assimilative capacity of the soil to treat and dispose of the applied wastes and (b) avoid adverse impacts to human health and the environment. In addition, any waste should be applied over such limited time spans and at such rates that no land is irreversibly removed from a defined use. After use for waste treatment, a land treatment site should be able to be returned to uses such as forest, open space, parks or crop production, unless it is to be dedicated as a site for disposal.

Schematically this concept is presented in Figure 1. When wastes are applied to land, parameters of environmental concern may increase. Examples of such parameters include nitrates in groundwater, metal accumulation in soils, and bioaccumulation of waste constituents in soil biota. At low waste application rates, although the amount or concentration of each parameter may increase, no adverse impacts result. However as the rate of waste application increases, environmental and human health standards and criteria may be approached or exceeded. Such limits represent the soil assimilative capacity for the waste based upon one or more waste constituents.

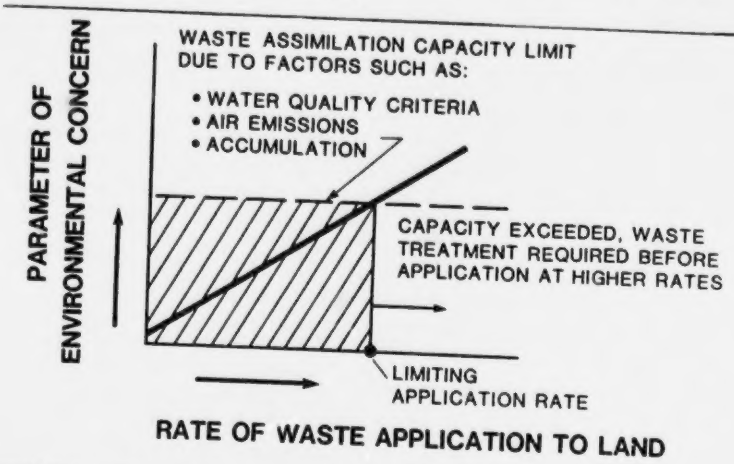
WASTE ASSIMILATION CAPACITY LIMIT DUE TO FACTORS SUCH AS:
• WATER QUALITY CRITERIA
• AIR EMISSIONS
• ACCUMULATION
CAPACITY EXCEEDED, WASTE TREATMENT REQUIRED BEFORE APPLICATION AT HIGHER RATES
LIMITING APPLICATION RATE
PARAMETER OF ENVIRONMENTAL CONCERN
RATE OF WASTE APPLICATION TO LAND

FIGURE 1. The window of acceptable conditions for a land treatment system is a function of specific limiting criteria such that the soil assimilative capacity is used but not exceeded.

In order not to exceed such limits, the waste application rate must not exceed the limiting application rate. To avoid exceeding certain limits, such as cumulative metal limits, waste application may have to cease. Higher application wastes may be possible if the waste to be applied receives preapplication treatment to reduce a specific constituent that may be limiting the waste application rate.

In Figure 1, the cross-hatched area represents the window of acceptable conditions for a land treatment system so that adverse human health and environmental impacts are avoided. At this time, adequate information is available on the soil waste assimilative capacity for inorganics, many organics and for pathogens.

To design or evaluate a land treatment system, information is needed on many factors. These include: (a) waste characteristics, (b) soil characteristics, (c) site characteristics such as slope, depth to bedrock, and depth to the groundwater, (d) vegetation to be grown (if any), (e) climatic conditions (precipitation, evaporation, and temperature) and (f) environmental criteria and standards. The proper evaluation of these and other factors results in application rates and scheduling that avoids adverse effects to human health and the environment and that stay within the window of acceptable conditions.

COMPARISON TO OTHER TREATMENT TECHNOLOGIES

Land treatment relies on the dynamic physical, chemical, and biological processes occurring in the soil. As a result, the applied wastes are degraded, transformed to nondetrimental by-products or immobilized. These processes are the same as those that occur in conventional municipal and industrial waste treatment systems. A major difference is that with land treatment, the processes occur in an unconfined reactor filled with soil particles while with conventional systems the processes occur in separate tanks filled with a liquid or slurry. The land treatment process can be compared to conventional waste treatment processes to illustrate the similarities and differences.

A conventional wastewater treatment system meeting permit conditions will consist of the following processes: sedimentation, biological treatment, and sludge stabilization and disposal. Where needed, tertiary treatment systems may include some combination of nutrient removal, adsorption, ion exchange, filtration, and chemical precipitation.

All of these processes occur automatically when land treatment is used. A land treatment site is a biological-physical-chemical reactor that contains: (a) particles (soil) that filter the applied wastewater and transform (adsorb, exchange, precipitate) many of the applied chemicals, and (b) bacteria and macroorganisms (earthworms, etc.) that stabilize the applied organics. In addition, a land treatment site may include vegetation that can utilize applied nutrients and inorganics during growth. One important difference is that with land treatment, there is no sludge that requires subsequent treatment and disposal. Any increase in biomass that occurs remains in the soil and undergoes natural degradation until it is stabilized and becomes part of the soil humus.

Compared to other treatment and disposal technologies, a properly designed and managed land treatment system has relatively low health and environmental liabilities. The wastes are applied intermittently (intervals can range from days for wastewaters to many months for sludges and industrial residues) and are incorporated in the surface soil. Movement of the applied constituents and of the net precipitation and any applied water is slow, and detention times in the soil are long. Under such conditions, slow as well as rapid degradation and immobilization reactions can be important in controlling the applied organics and inorganics. It is not unusual to have greater mass and percentage removals of waste constituents at a land treatment site than in conventional waste treatment systems.

As a result of the slower movement and longer detention times in the soil, changes in the characteristics of the soil, pore water, and groundwater are not rapid; monitoring can detect trends in any changes; and management adjustments can be made to minimize developing problems. In addition, if the land treatment system is well managed, maintenance and cleanup responsibilities are considerably less than with other waste disposal options.

In summary, land treatment is a controlled and managed treatment and disposal technology. It is an active and dynamic technology that is used to degrade and immobilize applied constituents. Land treatment should not be confused with passive storage technologies such as waste piles, surface impoundments, landfills or deep well injection. The design goals, long-term impact, and degree of treatment of these other terrestrial systems are very different from those of land treatment.

RELEVANT REACTIONS

A variety of processes influence the fate of waste constituents in land treatment systems. These include physical and chemical processes such as leaching, adsorption, desorption, photodecomposition, oxidation, hydrolysis, and biological metabolism by plants and soil microorganisms. The physical, chemical, and biological properties of the waste constituents and the soil interact with site-specific variables to influence the fate of the waste constituents in the soil. Subsequent papers in these proceedings provide details on many of the transformation and transport processes that determine the fate of constituents applied to the soil. The purpose of this section is to briefly summarize the major processes that affect the organics and inorganics applied to a land treatment facility.

Degradation and Loss

Decomposition of waste constituents added to soil may occur: (a) by chemical reactions with the soil, (b) as a result of biological degradation by soil microorganisms, or (c) as a result of photochemical degradation of organic wastes applied to surface soils.

Two common chemical reactions in soils are hydrolysis and neutralization of organic and inorganic compounds. Chemical reactions generally are not differentiated from biological reactions when the removal of organic compounds is measured in soil systems and quantification of chemical reaction rates is rare.

The importance of photochemical reactions will depend upon the method of application and of soil incorporation. If chemicals are applied to the site by surface application, they will be subjected to some photolytic action during their residence time on exposed plant and soil surfaces. If they are incorporated into the soil without subsequent tilling, photolytic degradation will be minor since sunlight does not penetrate deeply into the soil surface.

Microbial processes are usually the dominant soil decomposition mechanisms for organic waste constituents. The major concern usually is with the disappearance of organic constituents considered detrimental. The disappearance frequently is cited in terms of the half-life of a compound in the land treatment site or under defined conditions. The term half-life is used to indicate the persistence of a chemical in the soil, water or air environment. The half-life of a compound is the time required for its concentration to decrease to one half of its initial value. Half-lives can be estimated from first-order kinetics if first-order rate constants are known for waste constituents. The time required for the compound to decrease to any fraction of its initial level also can be estimated if the appropriate rate constants are known.

Performance data indicates that the degradation of most chemicals in the soil can be adequately modeled using a first-order reaction ($dc/dt = -KC$). The model indicates that at any one time, t, the rate of degradation is proportional to the concentration C of the chemical in the soil. First-order kinetics generally apply where the concentration of the chemical being degraded is low relative to the biological activity in the soil, such as in a land treatment site. The half-life of specific compounds varies substantially and can range from very rapid (half-life of minutes) for readily degradable compounds such as amino acids and sugars to very slow (half-life of months or years) for some polynuclear aromatics.

Due to the volatile nature of some organics in the applied wastes, emissions of these materials by vapor transport from the soil may occur during land treatment. Volatilization is not considered an acceptable treatment method in and of itself. The driving force for volatilization results from the vaporization of a chemical within the soil pore space. The volatilization rate of a chemical is strongly affected by its adsorption to soil organic matter and its solubility within the soil water. Volatilization losses are affected by waste, soil, and site specific parameters.

Immobilization

A considerable body of data exists concerning the immobilization of metals at land treatment facilities. Metal retention in the soil is a function of the metallic compounds such as hydroxides, that are formed, the organic and clay content, the pH, and the oxidation/reduction potential of the soil. The mechanisms of retention include specific adsorption, cation exchange, substitution in the clay structure, precipitation, and co-precipitation.

Adsorption is the predominant mechanism of metal immobilization. Soil pH has an important role in controlling metal solubility. Low pH values decrease the adsorption of metals to pH-dependent specific adsorption sites on mineral surfaces, and lower the CEC of soil organic matter. The soil pH that minimizes metal uptake by plants generally is greater than 6.5.

The cation exchange capacity (CEC) is a soil property that is related to the retention of metals in soil. A direct relationship between CEC and metal retention has been difficult to establish, and CEC is best interpreted as a general indicator of the ability of soil to limit metal solubility.

The CEC of a soil is associated with the silica and alumina components in clays and the phenolic and carboxylic groups associated with soil humus. Typical CEC values for uncontaminated soils range from 2–4 meq/100 g for sandy soil, 4–10 meq/100 g for sandy loams, 10–15 meq/100 g for loams, 10–25 meq/100 g for silt loams, and 20–60 meq/100 g for clay and clay loams.

Summary

The soil is not an inert desert. Rather, it is a matrix of pore spaces and solid matter that interacts with natural residues and the residues of human activity that are applied to it. The solid matter consists of mineral particles derived from rock and of organic matter resulting from the decay of plant and animal tissue. In addition, the soil contains myriad microorganisms and macroorganisms. As a result, there are numerous dynamic physical, chemical, and biological processes that occur in the soil to degrade, transform, and immobilize detrimental constituents in the applied wastes.

Proper utilization of these processes so that the assimilative capacity of the soil is not exceeded will result in a land treatment facility that is acceptable, environmentally sound, often cost effective, and that can be utilized for the treatment and disposal of diverse wastes.

HAZARDOUS WASTE LAND TREATMENT

General

Land treatment is used for the treatment and disposal of hazardous wastes. In a survey of hazardous waste land treatment facilities, 197 were identified (7). Over half were associated with petroleum refining and production and about 15% were associated with chemical production. The geographical distribution of these facilities was broad with most concentrated in the southeastern states from Texas to the Carolinas. The majority of those identified were less than twenty-five acres in size.

Pertinent Regulations

The Environmental Protection Agency (EPA) is required by the Resource Conservation and Recovery Act (RCRA) to issue standards applicable to the owners and operators of hazardous waste management facilities. These standards are to be used in issuing permits for facilities that treat, store, or dispose of hazardous waste. These regulations contain a groundwater protection standard and design and operating requirements for each type of land disposal technology.

Hazardous waste land treatment units are one of the disposal technologies for which standards were issued in July 1982 (8).

The owner or operator of a hazardous waste land treatment unit (HWLT) must establish a program to ensure that hazardous constituents placed in or on the soil are degraded, transformed, or immobilized within the treatment zone. The regulations define the principal elements of a HWLT program as: (a) the wastes to be applied, (b) the design and operating measures necessary to maximize degradation, transformation, and immobilization of the hazardous waste constituents and (c) an unsaturated zone monitoring program. The maximum depth of the treatment zone must be: (a) no more than 1.5 meters (5 feet) from the initial soil surface and (b) more than one meter (3 feet) above the seasonal high water table.

For each waste that will be applied to the treatment zone, the owner or operator must demonstrate, prior to the application of the waste, that hazardous constituents in the waste can be completely degraded, transformed, or immobilized in the treatment zone. The treatment demonstration is required to establish that the combination of operating practices at the HWLT site will, as a result of the waste characteristics and the soil and climate characteristics at the site, be protective of human health and the environment. The treatment demonstration will be used to determine permit requirements for the wastes to be applied and the operating principles to be used. A draft manual providing guidance for such treatment demonstrations has been developed (9).

HWLT units also must have a groundwater monitoring program. The goals of such a program are to detect and correct any groundwater contamination. The regulations also set forth requirements for runoff and run-on controls, for growth of food chain crops on such sites, for closure and post-closure care, and for record keeping.

The preamble to the July 1982 regulations (10) indicates that EPA believes that land treatment can be a viable management practice for some types of hazardous wastes. However, the success of such land treatment units depends on the operational management of the facility, hence the reliance on proper design and operating measures, on the unsaturated zone monitoring and on the treatment demonstration. The basic criterion to be used in evaluating a treatment demonstration is that it must be possible to achieve complete degradation, transformation (into nonhazardous constituents) or immobilization of the hazardous waste constituents in a HWLT facility. It is recognized that it will not always be possible to achieve 100% "treatment" at an operating facility because of variations in climatic or other conditions not under the control of the HWLT owner or operator.

The Resource Conservation and Recovery Act was amended in 1984 (11) (PL 98–616). These amendments represent a dramatic shift in national policy concerning hazardous waste land disposal options. Through the amendments, Congress is attempting to mandate a regulatory program that will force hazardous waste management efforts away from conventional land disposal methods and towards recycling, waste reduction, and treatment. These changes are in a response to a perception that contamination of our water and the environment may be more severe than previously expected. There is mounting evidence that groundwater contamination from waste storage units and improper hazardous waste disposal is increasing and causing health and environmental threats.

Certain wastes are to be prohibited from conventional land disposal and deep well injection. In addition, the amendments include statutory deadlines that will prohibit the land disposal of all listed hazardous wastes unless EPA determines that the prohibition on one or more methods of land disposal for a waste is not required to protect human health and the environment for as long as the waste remains hazardous. The factors to be taken into account in making such a decision are: (a) the long term uncertainties associated with land disposal; (b) the goal of managing hazardous waste in an appropriate manner; and (c) the persistence, toxicity, mobility, and propensity to bioaccumulate of such hazardous wastes and their hazardous constituents.

The amendments define land disposal as placement of hazardous waste in a landfill surface impoundment, waste pile, injection well, land treatment facility, salt dome formation, salt bed formation, or underground mine or cave. Thus, land treatment is one of the land disposal methods that is to be scrutinized as to its effectiveness in protecting human health and the environment when used with hazardous wastes.

When EPA prohibits one or more methods of land disposal for a particular hazardous waste, the amendments require simultaneous promulgation of regulations specifying levels or methods of treatment, if any, which substantially diminish the toxicity of the waste, reduce its likelihood of migration, and reduce the long term threat to human health and the environment. In the event such a waste is treated to the level or by methods specified in such regulations, the waste may be disposed of in a land disposal facility meeting the minimum technological requirements.

Finally, with regard to the land disposal of hazardous wastes, the amendments address air emissions from hazardous waste facilities. EPA is required to promulgate regulations for the monitoring and control of air emissions at hazardous waste treatment, storage, and disposal facilities by May 1987.

EPA has efforts under way to determine which land disposal methods are protective of human health and the environment when used with specific wastes. These efforts are in the early stages of development, and it is too early to predict how land treatment will be identified, i.e., as a technology that is protective or one that is unacceptable when used with certain hazardous wastes.

For certain wastes, there are treatment and disposal technologies that are more appropriate than land treatment. For example, concentrated solvents should be recycled or used as a supplemental fuel and halogenated compounds that bioaccumulate such as PCB and PBB should be disposed of in another way. The criteria for determining the treatability of a waste in a land treatment facility will involve an evaluation of the degradability, mobility, and potential bioaccumulation of the waste constituents. If waste constituents are sufficiently volatile or mobile or have a propensity to bioaccumulate at a land treatment site such that there is an adverse impact to human health and the environment, then the wastes should not be land treated.

SUMMARY

The 1984 RCRA amendments have had a significant impact on the feasibility of using land treatment for hazardous wastes. The amendments were intended to control the migration of constituents that have an adverse impact on human health and the environment. The major focus is on land disposal methods such as landfills, waste piles, surface impoundments, and injection wells in which the assimilatory capacity of the soil is either not used for control and management of the wastes or is exceeded by the load placed on the soil.

Land treatment is a technology that uses but does not abuse the assimilative capacity of the soil. It also is a technology that avoids adverse impacts to human health and the environment through proper design, management, monitoring and closure. The design and operating requirements for any land treatment facility, including those used to treat hazardous wastes, are focused on: (a) maximizing the treatment of the applied constituents by degradation, transformation to non-detrimental constituents, and immobilization processes in the treatment zone; and (b) minimizing the release of detrimental constituents to the environment.

With regard to hazardous wastes, it is still an open question as to whether land treatment should be considered as a treatment process that is protective of human health and the environment or as a disposal process that may be an inappropriate technology when used with hazardous wastes. Available information, such as from the land treatment of petroleum industry wastes (6), suggests that land treatment should be considered as the former (protective of human health and the environment) rather than the latter (nonprotective) type of a technology.

The purpose of this conference is to summarize the available knowledge on this topic. The presentations will: (a) describe the transport and fate of organics and inorganics applied to land treatment systems; (b) identify the degradation, immobilization, volatilization, and bioaccumulation that occurs when wastes are land treated; (c) indicate monitoring approaches that are appropriate for unsaturated and saturated soils; (d) review current federal and state regulations and guidelines; (e) summarize current research and studies; and (f) present case studies of existing land treatment systems. These presentations will clarify the extent to which land treatment for industrial wastes, and especially hazardous wastes, can be protective of human health and the environment.

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TRANSPORT AND FATE PROCESSES IN THE SUBSURFACE

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ABSTRACT

The three processes most likely to affect the fate of trace level organic contaminants (TLOs) in groundwater are: 1) the flow regime; 2) sorption to soil organic matter; and 3) biodegradation. Each will be reviewed with emphasis on recent progress. The hydrologic flow field must be understood first, where the most important variables are the groundwater velocity and advective transport, but in highly nonhomogeneous aquifers, dispersion may cause contaminants to appear at observation wells in order of magnitude or more sooner than expected based upon average velocity. Furthermore, recent theory and experimental results suggest that dispersion effects may vary with distance from a contaminant source. The consequences of these notions will be discussed qualitatively.

Sorption to soil organic matter normally is proposed to be the primary physicochemical process attending the fate of TLOs in groundwater. This retardation effect has been related to normally reported octanol/water partition coefficients via simple log/log relationships. For the more water soluble TLOs (~100 mg/l or greater water solubility), the octanol/water partition relations probably apply. Three aspects may alter these simple relations: dissolved organic carbon (DOC), flow velocity, and slow sorption kinetics. The effect of each of these on the sorption of TLOs will be discussed.

Finally, slow biodegradation of TLOs may be a significant fate mechanism that previously had been ignored in groundwater studies. Depending on whether an aquifer is aerobic or anaerobic and the nutrient levels in the groundwater, most organics appear to be degradable in the time frame associated with groundwater flow. The classes of compounds which are degraded only in aerobic or anaerobic aquifers will be discussed and examples presented.

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GROUNDWATER HYDROLOGY

An understanding of the hydrologic characteristics of a particular waste site is a necessary requirement before any other mechanisms of chemical transport or biological decay can be explained. Many excellent textbooks exist which provide more detail on groundwater flow and well mechanics (DeWiest 1965; Bear 1979; Freeze and Cherry 1979).

Groundwater flow predictions began in a systematic way with Darcy's Law in 1856. Darcy studied the movement of water through sand beds and found the flow rate to be proportional to the difference in "head" between the two ends of the bed. The flow is directly proportional to the hydraulic gradient and to the proportionality constant, k, the hydraulic conductivity, which is dependent on the nature of the porous medium. The ratio of the change in hydraulic head (Δh) to the distance of water flow (Δl) is referred to as the hydraulic gradient.

Darcy's Law can be extended through use of the velocity potential φ. The velocity potential is related to hydraulic head, h, multiplied by the hydraulic conductivity. It is shown in standard texts that φ can be combined in a particular way with the stream function ψ to create an orthogonal set of equipotential lines and streamlines in an aquifer (Figure 1). Such patterns are referred to as flow nets for groundwater flow in porous media, and represent a useful analytical tool for steady-state, two-dimensional flow problems.

It is necessary to define the hydraulic head at various points in the field using a piezometer or well. At the point where a well intersects the water level in a shallow aquifer, water in the piezometer will rise to the water table. In the case of an artesian aquifer, water will rise to the piezometric level. By interconnecting a series of well levels together as contours of constant equipotentials, the piezometric surface can be generated. Velocity or streamlines will be perpendicular to the equipotentials and will flow in the direction of the gradient (from higher toward lower head values).

Aquifer systems can be classified as unconfined (shallow water table) or confined (under pressure). Parameters of concern include hydraulic conductivity (k), porosity (n), storage coefficient (S), and thickness (b) for confined aquifers. Storage coefficient (S) is the volume of water that a permeable unit will recharge or discharge from storage per unit surface area per unit change in head (dimensionless). In an unconfined aquifer, as the water level falls, water drains from the pore spaces; this storage release is referred to as specific yield (S_y). Transmissivity is the product of hydraulic conductivity and saturated thickness for a confined aquifer.

An aquifer is considered homogeneous if it has the same hydrogeologic properties at all locations. In heterogeneous formations, hydraulic properties change spatially as in the case of layered sediments. A unit is isotropic if there are no directional variations of hydrologic parameters. Directional fractures can cause a unit to be anisotropic.

All of the above properties of aquifers are important when assessing the migration of contaminants which may move laterally or vertically from a waste site. Hydraulic conductivity and source head values are most important in determining overall flow rates and directions of migration. Clay liners or slurry walls have

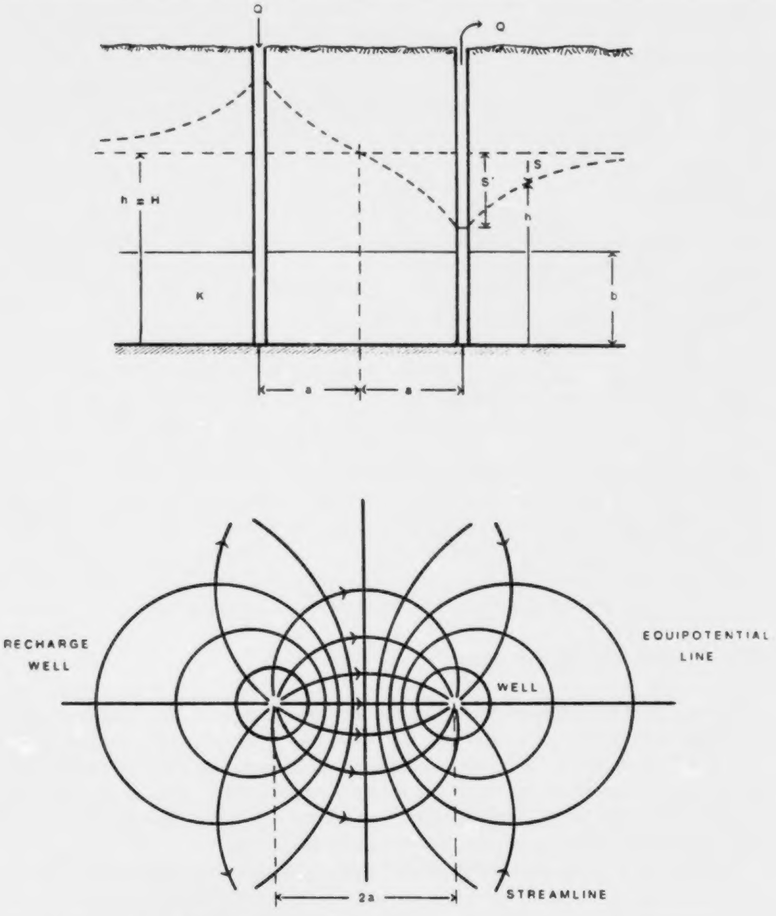
Q
Q
h = H
S'
S
h
K
b
a
a
RECHARGE WELL
EQUIPOTENTIAL LINE
WELL
2a
STREAMLINE

FIGURE 1. Flow pattern for injection-production doublet (DeWiest 1965).

been used in recent years to increase the resistance to flow in porous media and to help control leakage of hazardous wastes.

Well Systems

Well pumping or injecting systems have a major effect on groundwater hydrology and hydraulics. In particular, pumping wells cause a cone of depression of the piezometric surface and therefore increase flow rates to that point. In the same ways, injecting wells create a positive pressure above background which forces movement out, generally in a radial direction. The subject of well hydraulics is at an advanced state of knowledge and many analytical solutions have been evaluated in radial coordinates for one or more wells (injecting or pumping). Figure 1 presents the equipotential and flow lines for the doublet which is often used in field tests for tracer breakthrough and aquifer analysis.

Pump tests on a single well or well field can be used to quantitatively evaluate hydraulic conductivity k and storage coefficient S for an aquifer. Either steady-state or transient equations are available to perform these calculations, and if the aquifer is relatively homogeneous and isotropic, results of these tests can be quite accurate. Problems can occur where no-flow boundaries, constant head boundaries, or leaky aquitards are present.

Pumping or injecting wells can be designed to hydraulically control, remove, or contain an existing waste plume. For those cases where the aquifer can be easily pumped and the contaminant can be treated, a withdrawal well system can be used to transport the contaminant to a treatment plant. Another possible strategy is to pump out at the down-gradient end of a waste plume, treat above ground, and reinject the treated water up-gradient of the plume (Figure 2). The second strategy has the advantage of speeding up the flow rates and clean-up time compared to the passive pumping. In certain cases where a waste plume is in a relatively "tight" aquifer formation, an injection array of wells may be used to hydraulically contain the waste until such time as it can be physically dug up and removed, slowly pumped out, or microbially degraded (Figure 2).

Mass Transport Processes—Advection

Once a flow field has been established adjacent to a waste site and the hydrogeology is relatively well understood, mass transport of contaminants can be evaluated. Well hydraulics and groundwater hydrology are more advanced sciences than either mass transport or degradation processes; thus, even if a flow field is extremely well defined, there is no guarantee that an accurate prediction of contaminant levels in a waste plume can be achieved.

The Darcy velocity presented earlier must be adjusted by porosity in order to calculate average pore or seepage velocity, since contaminants migrate at the pore velocity. If the flow field is a complex, heterogeneous pattern, then mass transport calculations will only be as accurate as the knowledge of the velocity field variations. Movement of a contaminant with the bulk fluid according to the average pore velocity is called advection. In a homogeneous, isotropic aquifer, advective transport may be the dominant mechanism of migration if the velocity field is due to a large gradient. In such a case, the contaminant front (or wave) produced by a continuously leaking source would appear as a step function in one-dimension (Figure 3). The time of arrival of the step response would coincide with the length of travel divided by the average pore velocity.

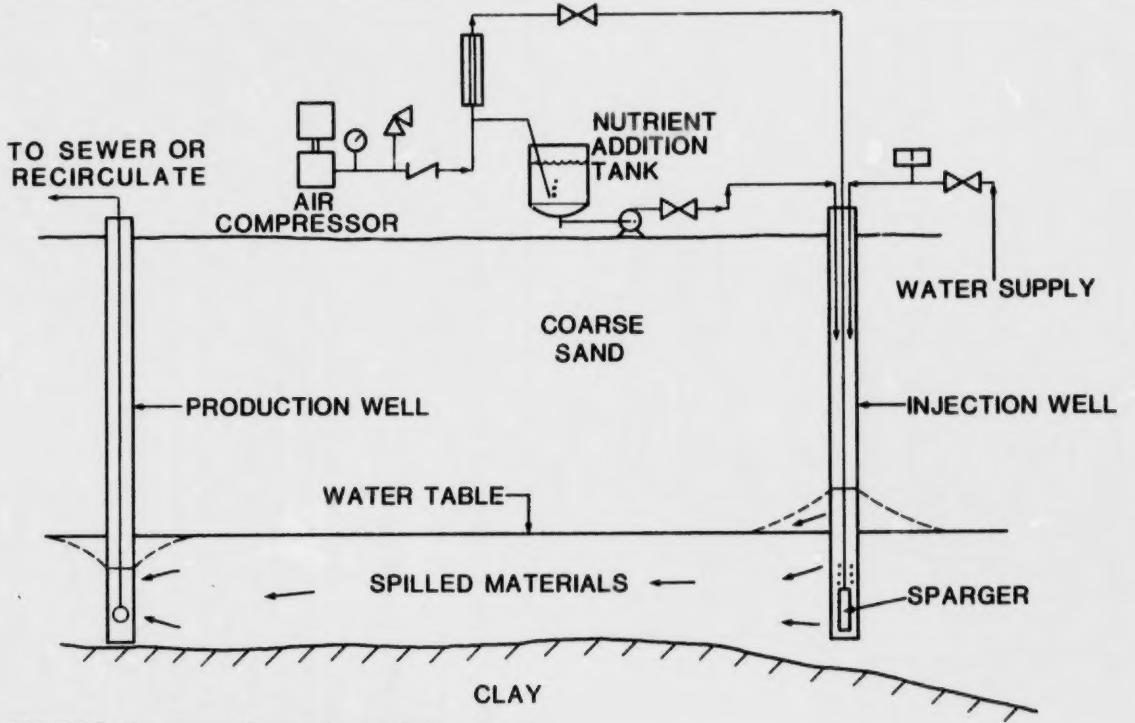
TO SEWER OR
RECIRCULATE
AIR
COMPRESSOR
NUTRIENT
ADDITION
TANK
WATER SUPPLY
COARSE
SAND
PRODUCTION WELL
INJECTION WELL
WATER TABLE
SPILLED MATERIALS
SPARGER
CLAY

FIGURE 2. Treatment schemes above or below ground.

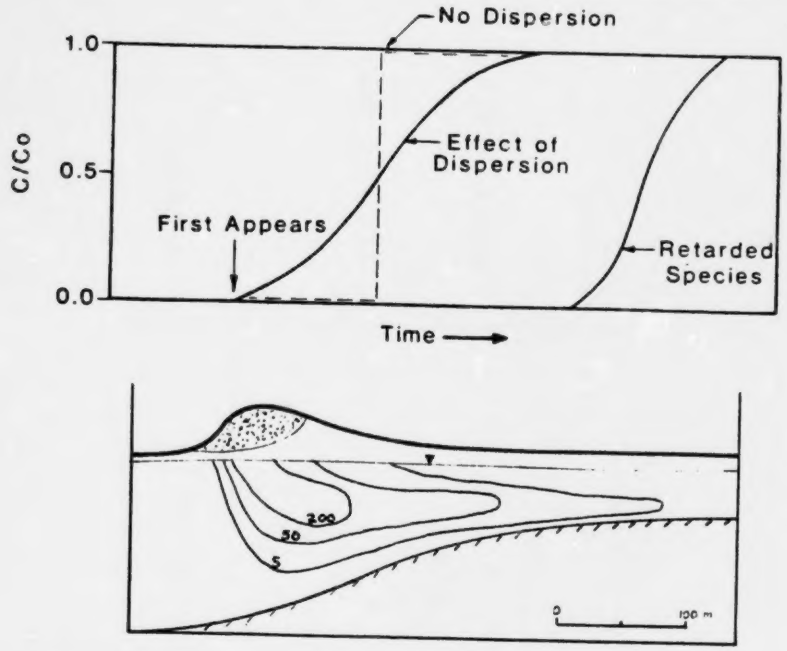

FIGURE 3. Effects of dispersion in one and two dimensions.

Dispersion Mechanism

The dispersion process is described in detail by Bear (1979), Anderson (1979), Freeze and Cherry (1979), and more recently by Anderson (1984) and Gillham et al. (1984). Dispersion refers to the spreading of a stream or discrete volume of contaminant as it flows along in an aquifer. For example, as a slug of tracer (chloride) moves along with average velocity in the x-direction, longitudinal spreading or dispersion will occur parallel to the y and z axes (Figure 3). Dispersion causes mixing with the surrounding volume of groundwater and is, therefore, a mechanism for dilution. Greater spreading occurs then due solely to advective transport, and this additional spreading is of concern for toxic or hazardous waste plumes. Arrival times of contaminants at adjacent water supply wells may be shorter due to dispersion in the direction of groundwater flow.

It is now generally recognized that the presence of heterogeneities in the subsurface is largely responsible for the appreciable spreading of contaminants documented in a number of field studies (Anderson 1979). Dispersivity, α, is defined as a characteristic mixing length and is a measure of the spreading of a contaminant. When α is multiplied by average pore velocity in one dimension, the product is referred to as dispersion coefficient, D_L. Laboratory column studies yield values of α from 1 to 10 cm, while field studies produce values from 3 to 200 m (Anderson 1979). Tracer tests have been used recently to evaluate α (both longitudinal and transverse) in field settings. Transverse dispersivity typically ranges from 1 to 10% of longitudinal dispersivity, which explains the elongated shape of most waste plumes.

Recently, new attention has been directed towards the uncertainty surrounding the measurement and use of the dispersion coefficient in field sites (Anderson 1984). The traditional approach has been to represent dispersion by an expression according to Fick's law of diffusion

$$\text{Mass Flux} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right)$$

where c is concentration, D_{ij} is dispersion tensor, and i,j refer to cartesian coordinates. D_{ij} is the sum of mechanical dispersion and molecular diffusion, but in many field problems, molecular diffusion can be neglected. Recent work indicates that the process may not follow the mass flux equation until the travel distance exceeds hundreds of meters or more from the source in porous media (Smith and Schwartz 1980; Gelhar and Axness 1981). Several researchers have noted an apparent increase in dispersivity with distance from the source, or a non-Fickian mechanism (Pickens and Grisak 1981).

The above results are different from many of the earlier reports on modeling of mass transport at field sites prior to 1979, where dispersivity was assumed constant. The new challenge is to develop a transport model which includes variable dispersion parameters which can be practically determined. Carefully designed field tracer tests are needed to further evaluate the dispersion process through space and time.

The above complexities may not be completely solved in a reasonable time period due to a lack of good data and understanding of the complex dispersion process. In the meantime, existing models of mass transport which include advection, constant dispersivity, and other chemical and biological terms will continue to be used. It may be that processes of organic adsorption and microbial degradation are even more complicated and may dominate the observed plumes at hazardous waste sites. For sites in which advection is a dominant mechanism, the effect of variable dispersivity may be slight. In systems where pumping or injecting of fluids is occurring, advective models exist to accurately describe the flow and mass transport.

Other sections in this paper describe the mechanisms of chemical adsorption, reaction, and microbial degradation. These mechanisms may be more important than dispersion in certain cases, and may be more predictable in other cases. However, a good understanding of the flow field and hydrogeology is prerequisite to any further evaluation of transport mechanisms which may be operating at a waste site.

SORPTION MECHANISMS

Sorption of trace ogranics to soil organic matter is generally proposed to be the primary physicochemical mechanism for altering the fate of such organics in saturated groundwater flow. A chromatographic partitioning process is commonly used in soil studies to model the average velocity of a compound, V_c, relative to the average velocity of water, V_w. Applying the theory of chromatography to saturated groundwater systems, the ratio, $R = V_w/V_c$, can be shown to be approximately (Waggett 1984):

$$R = \frac{V_w}{V_c} = 1 + \frac{\rho b}{n} K_p \tag{1}$$

where ρb = bulk density of aquifer (about 2 g/cm^3)
n = porosity

$$K_p = \frac{\mu\text{g of compound/g-soil phase}}{\mu\text{g of compound/ml-water phase}}$$

For any given soil and trace organic, the partition coefficient K_p can be determined by mixing an appropriate amount of soil and water spiked with the compound and measuring the concentration of trace organic in each phase at equilibrium. This would require separate measurements for each soil/trace organic compound pair. Fortunately, methods have been developed, as will be outlined in the following paragraphs, to estimate the K_p values for nearly any trace organic compound based upon a single measurement of the soil phase organic carbon content (OC).

While studying the fate of pesticides, soil scientists observed that for most compounds a soil independent partition constant K_{oc} would be obtained if the partition coefficient K_p were divided by the weight fraction organic carbon in the soil:

$$K_{oc} = K_p/OC \tag{2}$$

$$OC = \text{g-organic carbon/g-soil phase} \tag{3}$$

Often the OC value is reported in terms of "organic matter" by multiplying the measured organic carbon value by a factor of 1.7 to 1.9. At least three assumptions are implicit in this adsorption model: (1) trace organics in the water are at equilibrium with the soil organic phase; (2) only the soil organic matter adsorbs trace organics; and (3) all soil organic matter is the same, regardless of soil type or vegetative source. Each assumption will be briefly discussed.

The first is called the "local equilibrium" assumption and implies that the process of partitioning of TLOs between the aqueous and soil phases is at equilibrium at all points in the flowing aquifer. (For a mathematical statement of this critical assumption, see Freeze and Cherry 1979, P. 402 or Ruthven 1984, Chapter 8.) For this assumption to be valid the seepage velocity of water must be below some critical value. Estimates of this critical maximum velocity are 10^{-4} cm/sec (Schwartzenbach and Westfall 1981), 10^{-3} cm/sec (James and Rubin 1979) and 10^{-3} cm/sec (Waggett 1984), but from Karickhoff (1979, 1984) it can be suggested that this velocity may depend inversely upon the water solubility of a compound.

The second assumption appears to be valid for OC values greater than about 0.0002 or 0.02% OC (Schwartzenbach and Westfall 1981). At lower OC values the sorption due to the mineral phase begins to predominate.

The third assumption, that all organic matter is the same, is particularly surprising at first consideration, but is consistent with the hydrophobic theory of solubility (Tanford 1980). The hydrophobic theory suggests that the relative solubilities of hydrocarbons in water are controlled by the relative repulsion of the TLO molecules by the polar water hydrogen bonding network and not by the affinity of the hydrocarbon molecule for a hydrocarbon or lipid phase. The validity of this assumption is further supported by experience with numerous soils (Hamaker and Thompson 1972 and Karickhoff 1979).

To further simplify matters, the soil independent K_{oc} value (Equation 2) can be related to the commonly reported or easily calculated octanol/water partition coefficient, K_{ow}:

$$K_{ow} \equiv \frac{C_o}{C_w} \tag{4}$$

where C_o and C_w refer to the concentrations of a TLO compound in octanol and water, respectively. Karickhoff (1979) showed that for a suite of neutral TLO compounds variation in solubility of about 10^6, the relation between K_{oc} and K_{ow} was:

$$K_{oc} = 0.62\,K_{ow} \qquad r^2 = 1.00 \tag{5}$$

Finally, Lyman (1982) related the K_{oc} values to the water solubility, S(mg/l):

$$\log K_{oc} = 0.55 \log S(\text{mg/l}) = 3.64 \tag{6}$$

Substituting Equations 2, 5, and 6 into Equation 1 yields, R in terms of K_{ow}:

$$R\,(V_w/V_c) = 1 + \frac{\rho b}{n}\,(0.62\,K_{ow}OC) \tag{7}$$

or, in terms of water solubility:

$$R\,(V_w/V_c) = 1 + \frac{\rho b}{n}\,(10^{3.64}\,S^{-0.55}OC) \tag{8}$$

The effects of various OC and S values on R are illustrated by constant OC isopleths in Figure 4 for a typical soil of $\rho b = 2$ g/cm^3 and $n = 0.3$. Using Equation 8:

$$\begin{aligned} \log R(V_w/V_c) &= \log\,(1 + 10^{4.42}\,S^{-0.55}\,OC) \\ &\cong -0.55 \log S(mg/1) + \log OC + 4.42 \end{aligned} \tag{9}$$

The average velocity of a trace organic compound of aqueous solubility S(mg/l) can be estimated for most aquifers using Figure 4 once the OC and V_w are determined. The coefficient $\rho b/n$ is generally about six and changes by about a factor of two for $n = 0.25$ to $n = 0.50$, which would move the isopleths in Figure 4 by only ±0.15 log units. Fertile top soil will generally have from 1 to 5% organic carbon, but groundwater aquifers often have from 0.01 to 0.2% organic carbon. It can be seen that only the extremely insoluble compounds such as DDT, benzo[a]pyrene, and some PCBs are expected to be "highly retained" by nearly all soils. For most compounds it will be necessary to determine OC before even qualitative estimations of the extent of retardation can be made.

The general usefulness of K_{oc} values in prediction of the fate of trace organics has been well established in recent years. Lyman (1982) has reviewed the current literature on methods to calculate K_{oc} values. Chiou and Schmedding (1982) discussed the theoretical background of various log/log relations in terms of the Hildebrand solubility parameters, δ, and the Flory-Huggins theory of polymeric solubility. Wilson et al. (1981) conducted a series of column experiments with 13 compounds such as chloroform, trichloroethylene, and mono-, di-, and trichlorobenzene. The soil used contained from 0.02 to 0.22% organic carbon which yielded theoretical retardation values from 1.2 to 7.0 using an equation similar to Equation 7 or using Figure 4. They also studied trichloroethylene in a corresponding field site. Both laboratory and field results agreed with predictions based upon K_{oc} to within about 20% with no discernible systematic bias. Similar agreement between theory and field measurement was obtained by McCarty et al. (1981) using chlorobenzene from a wastewater injection facility in Palo Alto, California. A detailed review of earlier work on the fate of pesticides in a variety of soils was done by Hamaker and Goring (1972). Bedient et al. (1984), while modeling the fate of selected trace organics associated with a creosote hazardous waste site near Conroe, Texas, found general agreement between observed and predicted retardations of naphthalene, 2-methylnaphthalene, and dibenzofuran relative to chloride as a conservative tracer. Similar results were obtained by Ehrlich et al. (1982) for naphthalene at a creosote site in Minnesota.

Only a few reports of the fate of the very insoluble compounds such as DDT and PCBs have been performed such that the retardation predictions can be quantitatively checked. Enfield et al. (1983) did a detailed study of the fate of DDT vs. depth. In that study, DDT moved orders of magnitude farther than would have been predicted based upon retardation equations. Extensive reviews of the fate of other low solubility pesticides indicate that the simple relations which hold for the more soluble trace organics do not hold for the very insoluble compounds, even at low water velocities. In fact, these "insoluble" compounds are reported to be both "irreversibly" retained by the soil phase and mobilized much farther than expected in flow systems. The apparent disproportionation of the fate of the "insoluble" neutral compounds into a more *and* a less mobile than expected portion suggests that at least two interaction processes are operative. One combined explanation to qualitatively account for the observed facts would be that a kinetically inert (i.e., quasi-irreversible) complex forms between these less soluble compounds and the humic matter in both the soil and the water phases. As flow proceeds, the soil-bound portion would be immobile and the dissolved humic-bound portion would move with the aqueous phase. The degree to which a compound might proportion between the mobile dissolved organic carbon and the immobile soil organic carbon fractions could be a sensitive function of the order in which the phases were brought into contact as well as the exact nature (e.g., rigidity, molecular weight distribution, surface charge, etc.) of the two humic materials in question.

Poirrier et al. (1972) observed that the solubility of DDT was increased 15,800-fold in the presence of 100 ppm DOC. Wershaw et al. (1969) reported the solubility of DDT to be increased by only a factor of 20 over distilled water by 0.5% sodium humate in solution; this may reflect a pH dependence or an error in the solubility value used for comparison. In that same report, Wershaw et al. (1969) stated that the phytotoxicity of herbicides may be reduced 100-fold by the organic matter in the soil. Carter and Suffett (1982) reported on the interaction of DDT with humates from various sources and on the calcium, pH, and ionic strength dependence of that interaction. Similar variation in the interaction of trace organics with humates from different sources was reported by Diachenko (1982) for hexachlorobutadiene.

West (1984) separated about 0.2 g humic materials from 2000 liters of groundwater by the Thurman and Malcolm (1981) method. Using the separated humic material, she measured the partition coefficients of a series of compounds, all with water solubilities less than 0.5 mg/l. From her measurements, the following correlation was obtained:

$$\log K_p = -0.923 \log S(\text{mg/1}) + 3.294 \qquad r^2 = 1.000 \qquad (10)$$

$$\text{with} \quad K_p \equiv \frac{\mu\text{g compound/g DOC}}{\mu\text{g compound/g water}}$$

In order to calculate the enhanced transport of trace organics by DOC, Equation 8 can be modified as shown by West (1984):

$$R(V_w/V_c) = 1 + \frac{K_{OC}(OC)\rho_s(1-n)/n}{1 + K_p \, DOC \, 10^{-6}} \qquad (11)$$

with DOC in mg/l units, OC as weight fraction, n = porosity, and ρs = soil solid density. Using Equations 6 and 10 to express K_{oc} and K_p in terms of aqueous solubility, S(mg/l and assuming $\rho s = 2.65$ g/ml, Equation 11 becomes:

$$R(V_w/V_c) = 1 + \frac{10^{4.06}\,(S^{-0.55})OC(1-n)/n}{1 + 10^{-2.71}\,(S^{-0.923})\,DOC} \tag{12}$$

The effect of various DOC levels on retardation is illustrated in Figure 4 explicitly for 1% OC and n = 0.33. Drinking water aquifers generally have DOC levels between 0.1 to 10 mg/l, but wastewater DOC values may be 300 mg/l or higher. From these typical DOC and OC values it can be seen in Figure 4 that mediated transport will begin to be a significant mode of transport for water solubilities of 0.1 to 1.0 mg/l and below. The maxima in the constant DOC curves are a consequence of the observed exponential dependences of K_{oc} and K_p on solubility, $S^{-0.55}$ and $S^{-0.923}$, respectively.

Numerous compounds of environmental interest such as PCBs, benzo[a]pyrene, dioxin, etc., have solubilities less than 0.1 mg/l and would be expected to be transported much farther in groundwater than the simple retardation equation would predict. No field data are yet available against which to test these predictions, but Leo et al. (1971) reported 17 log/log-linear correlations similar to Equation 10 for the sorption of neutral compounds to various proteins, enzymes, and biological tissues. If such insoluble compounds are transported long distances as soluble DOC complexes, trace organics might be slowly released at distance due to changes in the groundwater pH, metal content, or after pumping and treatment for domestic use. Studies to test these notions are currently in progress at Rice University.

BIODEGRADATION

Microbial metabolism is one of the most effective processes for the removal of organic compounds that have passed through the surface layer of soil. The presence of a microbial population at levels up to and greater than 106 organisms/g dry weight of soil has been demonstrated for several shallow aquifers, and it is likely that these populations exist elsewhere (Wilson et al. 1983a, Wilson et al. 1983b, Hirsch and Rades-Rohkohl 1983, Lee et al. 1984). A significant portion of the organisms found in these systems have been shown to be active (from 0.01 to 50%) by comparison of viable cells resulting from plate counts with direct counts and with measures of respiratory activity such as 2-(p-iodephenyl)-3-(p-nitrophenyl)-5-phenyl tetrazolium chloride (Balkwill and Ghiorse 1985). Microbes from subsurface systems have generally been small (<1 μm) coccoid cells occurring in clusters closely associated with clay particles (Wilson et al. 1983a), although much of the microbial activity may be in the groundwater phase (Thomas et al. 1985). Often the groundwater organisms are in nutrient-poor environments where oligotrophic organisms are predominant. Eucaryotes, including protozoa and fungi, are infrequent, but have been isolated from several aquifers (Balkwill and Ghiorse 1985).

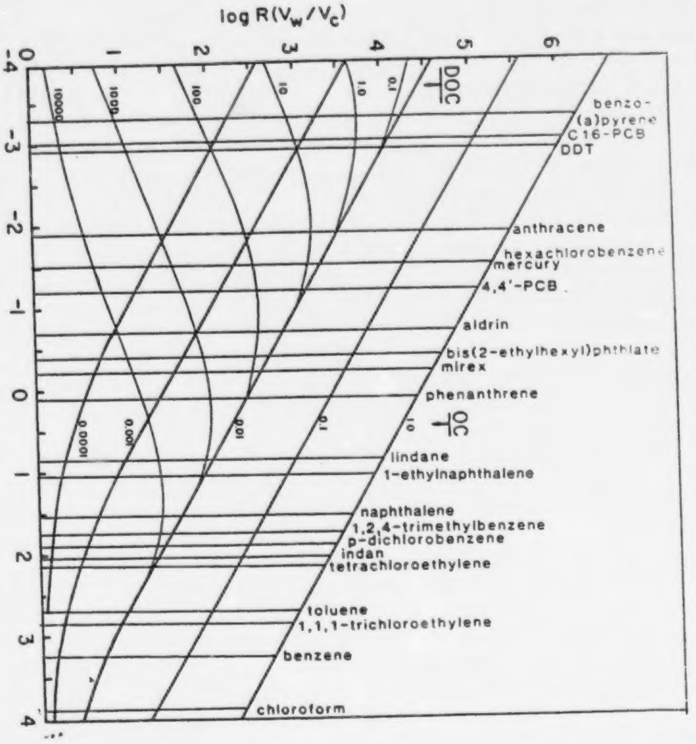

FIGURE 4. Plot of the retardation factor (R - $V_W V_C$) versus water solubility for trace organics at various constant soil organic carbon (OC) in weight fraction values and different levels of dissolved organic carbon (DOC) in mg/1. The OC isopleths are drawn for 0.0 mg/1 DOC. Various mg/1 DOC levels at 0.01 (1%) OC are included. The convex DOC isopleths can be moved straight up or down to intersect any given OC value of interest. The solubilities of a few typical trace organics are indicated by vertical lines. For example, the retardation factor for hexachlorobenzene in 100 mg/1 DOC water and 1% OC soil would be about $10^{2.5}$

Microbial metabolism of a contaminant can result in complete degradation of the parent molecule to carbon dioxide and water or incomplete biotransformation which yields other compounds. The organisms derive energy and produce and maintain cell mass by these biodegradation processes (McCarty et al. 1984). Oxygen (aerobic processes) or alternate electron acceptors (anaerobic processes) such as sulfate, nitrate, or carbon dioxide may be utilized in the groundwater environment depending upon the oxidation-reduction conditions of the aquifer. Aerobic conditions may allow the biodegradation of certain compounds, particularly aromatics, that are not susceptible to anaerobic metabolism. Some compounds such as the chlorinated aliphatics including chloroform, trichloroethylene, tetrachloroethylene, bromodichloromethane and dibromochloromethane are only degraded under anaerobic conditions. It has been suggested that biofilms are the predominant mechanism for the removal of organics from the subsurface. Biofilms result from the attachment of bacteria to solid surfaces where they can utilize the low levels of substrates in the groundwater. A minimum concentration of a substance may be required to support its biodegradation. However, secondary utilization or cometabolism may occur at levels below the critical minimum concentration provided that a primary substrate provides the energy required for maintenance of the cells.

Some compounds are likely to be resistant to microbial attack. Synthetic aromatic compounds often are recalcitrant (Hutchins et al. 1985). In general, compounds which have amines, methoxy, sulfonates and nitro groups, meta substitutions on benzene rings, ether linkages, halogens, and branded carbon chains are likely to be recalcitrant (Kobayashi and Rittman 1982). Typically, larger molecules are less degradable than smaller ones. The concentration of the contaminant is another important factor; very high levels of many compounds may be toxic and extremely low levels may not be sufficient to support microbial growth although cometabolic processes may allow some removal to occur (Hutchins et al. 1985). In a series of soil column studies, Hutchins et al. (1985) demonstrated that for trace level organics present in wastewater applied to rapid infiltration basins, the chemical characteristics of the compound are the most important consideration in determining if the compounds are degradable. If the compounds are labile and organisms are present which can degrade them, then biological processes will control their fate. For several of the wastewater organic constituents that were studied, a threshold concentration, usually between 0.01 and 0.1 μg/l, was found, and further degradation did not occur below this, regardless of whether or not the compound was being used as a primary substrate (Figure 5). Rates of mineralization were less than the rates of biotransformation, which shows that more refractory metabolites were probably being formed. Anaerobic conditions inhibited the biodegradation of compounds such as 2-(methylthio)-benzothiazole, benzophenone, p-(1,1,3,3-tetramethylbutyl)-phenol, 2-methylnaphthalene, o-phenylphenol and p-dichlorobenzene. These compounds, along with others, have been detected in groundwater adjacent to rapid infiltration sites.

Microorganisms from uncontaminated groundwater aquifers have been shown to be active against a variety of compounds ranging from styrene, chlorobenzene, toluene, and bromodichlorobenzene (Wilson et al. 1983a, Wilson et al.

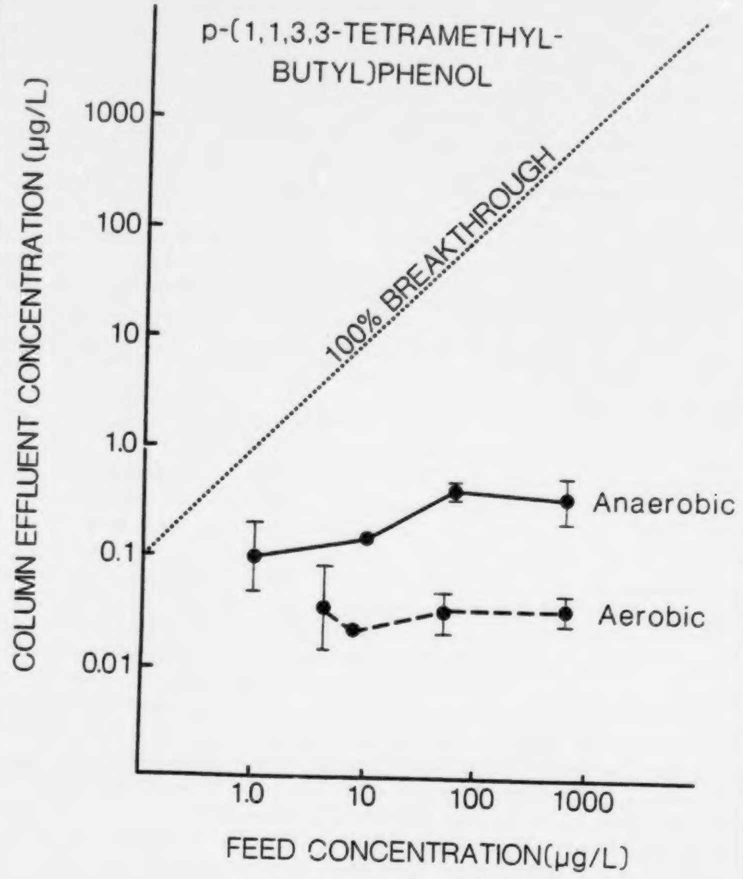

FIGURE 5. Breakthrough profile for p-(1,1,3,3,-tetramethylbutyl)-phenol during aerobic (– –) and anaerobic (—) operation or soil columns. Column effluent concentration is average ± standard deviation for two replicates.

1983b). Prolonged exposure of microorganisms to contaminants may allow the microbes to become adapted to such compounds. After this exposure, the microbes can metabolize such compounds which are not attacked immediately by microorganisms from pristine sites. Under aerobic conditions, rapid degradation of several aromatic contaminants was found in subsurface samples from contaminated areas of a site polluted by wood creosoting wastes, but no degradation of the contaminants was found in samples from background areas (Wilson et al. 1985). Adaptation to novel substrates was shown to occur within two days in an estuarine environment and lasted for varying periods (Spain and Van Veld 1983). Variations between sites and the microbial population's response to contaminants are likely.

Factors such as pH, salinity, terminal electron accepters, mineral nutrients, temperature, soil texture, toxicants (organics and heavy metals), and the presence or absence of the certain organisms may also limit the ability of microbial communities to degrade specific organic compounds. Research at a creosote contaminated site in Texas has shown that an adapted microbial population is present in the contaminated zones of the aquifer (Wilson et al. 1985, Lee et al. 1984). The biodegradation of the contaminants at this site, primarily aromatics, appears to be controlled by the concentration of dissolved oxygen in the groundwater (Lee et al. 1985). The addition of nutrients did not increase the overall removal of the contaminants greatly compared to the addition of dissolved oxygen alone, although the rates of biotransformation were increased somewhat (Table 1). In these laboratory experiments, batch systems containing groundwater from a moderately contaminated well were treated with nutrients plus oxygen and oxygen alone. Samples in which oxygen was made limiting and a sterile control were also run. Additional laboratory experiments were designed to determine the effects of oxygen concentration on microbial activity. Groundwater samples from a moderately contaminated well were sparged with nitrogen or air to adjust the dissolved oxygen content to between 1 and 2 mg/l and about 9 mg/l. In the presence of high dissolved oxygen, biotransformation of several of the aromatic hydrocarbons was rapid with rates up to 85% per day (Table 2). Microbial counts showed a concurrent increase. Biodegradation of individual compounds stopped when their concentrations were reduced to 0.005 to 0.03 mg/l even though oxygen remained, which indicates that microbial degradation may not be able to completely remove the contaminants. Dissolved oxygen levels as low as 1.5 mg/l supported microbial growth and degradation of the compounds, although at rates slower than under the higher dissolved oxygen level. The results of these experiments indicate that by increasing the dissolved oxygen at this site, microbial activity should be stimulated, the concentrations of the contaminants reduced, and the groundwater quality improved. Field tests also demonstrated a rapid response to the addition of dissolved oxygen (a drop from 4.0 to 1.0 mg/l within one day) with a concomitant reduction in the levels of organics.

This work shows that an active microbial population exists in the subsurface that is capable of degrading many of the contaminants that reach this environment. Adaptation to the contaminants may control the rate and extent of this biodegradation. The oxygen and nutrient levels in the aquifer play an important role in determining if the organic contaminants can be degraded by an adapted microbial population.

TABLE 1. Effects of nutrient and oxygen additions on rates and extent of biodegradation of polynuclear aromatics in groundwater.

Treatment	Naphthalene	2-Methyl Naphthalene	Dibenzofuran	Fluorene	Phenanthrene
		Biodegradation Rates (%/wk)			
A	54	52	57	54	57
B	58	56	37	33	29
C	23	16	11	0	17
D	0	0	0	0	*
		Percent Removal			
A	98	99	100	100	100
B	99	99	94	89	81
C	69	57	12	0	27
D	0	0	0	0	*

*Below detection limit of 1 g/l

Treatment:
A. Nutrient and dissolved oxygen addition
B. Dissolved oxygen addition
C. Oxygen limited
D. Sterile control

TABLE 2. Effects of dissolved oxygen concentration on biotransformation of polynuclear aromatic compounds in groundwater (% per day).

	High DO (9.0 mg/l)	Low DO (1.8 mg.l)
Naphthalene	72.7	30.7
2-Methyl naphthalene	48.8	31.6
Dibenzofuran	65.4	39.5
Fluorene	33.3	30.6
Phenanthrene	86.4	35.4

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LAND TREATMENT
BIOLOGICAL DEGRADATION PROCESSES

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An extremely important characteristic of land treatment is its capacity for effective and efficient biodegradation of waste constituents. This value of land treatment is exemplified by several noteworthy features which can take place during the process: (1) Soil microbial metabolism of wastes into mineral forms which directly enter natural elemental cycles. (2) Partial biodegradation (transformations) in the soil converting problem wastes into environmentally safe forms. (3) Biodegradation allows land treatment to function both as a *treatment* mechanism and a *disposal* process. Few waste management techniques offer such versatility. (4) In some instances soil bioconversions upgrade soil quality by increasing its natural organic content (humus).

This presentation focuses on major factors which influence biotransformation and biodegradation in the land treatment process, ways to maximize such events, biodegradation rates expected and finally, examples of biodegradation in operational land treatment systems. Municipal and agricultural wastes will not be addressed, although many of them are managed by land treatment.

THE BIODEGRADATION PROCESS

Biodegradation broadly means the decomposition of a compound into smaller pieces. More specifically, some use the term to mean a complete or ultimate breakdown, i.e., the mineralization of organic material. Others refer to biodegradation as the breakdown of a substance into components which are then routed into natural biochemical cycles regardless of size or ultimate fate of the degradation products. Still others use biodegradation to simply mean transformation of a substance into some innocuous or harmless form(s). In any case, for a given situation, biodegradation or biodegradability is actually defined by the analytical measurement(s) chosen. Thus, it is crucial to consider the measurements of biodegradation or biodegradability used when interpreting the significance of the process or characteristic of the material being addressed.

Microbial biodegradation is directly carried out by enzymes produced by microorganisms. Most enzymes are not released by the microbial cells necessitating that the substances to be degraded contact or be transported into the cell. Enzymes tend to be specific in reactions they mitigate so many may be required to complete a biodegradation sequence. Their production is genetically controlled, thus mutations and adaptations can alter the ability of the soil microflora to degrade a given material.

Microbial populations in soil are exceptional in their ability to attack and decompose organic substances and some inorganic materials. Soil bacteria, actinomycetes, and molds are present in large numbers; and their populations shift as necessary to metabolize added organic matter. As Loehr (1984) pointed out, the soil can be viewed as a large unconfined reactor which metabolizes matter added to it. Land treatment is a process designed to utilize this resource to our advantage in waste treatment.

MAJOR FACTORS WHICH INFLUENCE BIODEGRADATION IN LAND TREATMENT

Although soil is an extremely complex and variable environment, factors which influence biodegradation are the same as for other habitats. Some are subject to control while others are not, at least not practically so.

Chemical Structure of the Waste

Few organic substances are thought to be completely resistant to biodegradation strictly due to structure. However, there are numerous materials whose structures so strongly resist biodegradation they are usually considered to be nonbiodegradable. Generally such substances are high molecular weight cross linked polymers, highly branched hydrocarbons, or halogenated compounds. Some of these recalcitrant materials are naturally produced, and all are valued partially because of their resistance to deterioration. Examples of such materials are given in Table 1.

Other compounds are somewhat more susceptible to biodegradation yet are usually classified as nonbiodegradable. Such materials cause notable environmental problems and are not biodegraded rapidly enough to acceptably mitigate the problems. Examples of such materials are tetrapropylene alkylbenzene sulfonate ("hard" detergent) and penta-chlorophenol (antimicrobial).

Availability to Biodegradation

Water insoluble substances present difficult biodegradation problems for microorganisms since the organisms and their enzymes must function in aqueous solution. Therefore, some materials whose structures permit biodegradation are slow to be decomposed due to limited water solubility.

TABLE 1. Substances very resistant to biodegradation.

Natural Materials	Xenobiotics[1]
Kerogens	DDT (dichlorodiphenyltrichloeoethane)
Lignins	Kepone
Tannins	PCBs (polychlorinated biphenyls)
Humic substances	Ethylene dichloride
Coal	Polyethylene
Pristane	Vinyl chloride

[1] Chemicals foreign to living organisms.

One important advantage which land treatment offers for oil biodegradation is that the soil tends to hold the oil in place and provide large surface areas for its metabolism. This is in contrast to oil in aqueous environments.

Presence of Appropriate Microorganisms

The upper soil contains large numbers of microorganisms (Table 2) of extraordinary diversity. Routinely, microbiologists turn to the soil for cultures to test biodegradability or find unique microorganisms. Specially developed cultures are occasionally suggested for improving land treatment. The value of such products is highly questionable for three reasons: (1) If the waste is biodegradable, appropriate organisms are almost certainly already present in soil. Their populations and degradation efficiencies will increase when the waste is added. (2) "Foreign" microorganisms added to an environment such as soil are not likely to function well or even survive due to pressures exerted by the natural microbial population. (3) Specially developed characteristics in microorganisms tend to be unstable and lost with time and reproduction. Thus, there is little need to consider supplementation with different or additional organisms for effective land treatment.

Microbial Mass

If other factors are not limiting, the greater the functional microbial mass, the greater the rate of waste degradation. Usually, however, factors such as essential

TABLE 2. Microbial distribution in soil (Alexander 1977).

	ORGANISMS PER GRAM OF SOIL				
Depth (cm)	Aerobic Bacteria	Anaerobic Bacteria	Actinomycetes	Fungi	Algae
3-8	7,800,000	1,950,000	2,080,000	119,000	25,000
20-25	1,800,000	379,000	245,000	50,000	5,000
35-40	472,000	98,000	49,000	14,000	500
67-75	10,000	1,000	5,000	6,000	100
135-145	1,000	400	-	3,000	-

nutrients, substrate availability, or oxygen transfer limit population expansion. Attention to the controllable factors which influence biodegradation in the soil allows attainment of an effective microbial mass which will fluctuate according to food availability.

Concentration of Waste

Biodegradation of wastes added to soil at reasonable concentrations reportedly follows first order kinetics, meaning that degradation rate increases with increasing waste concentration (McGill 1980 and API 1984). See Figures 1 and 2. However, waste loading must be tempered to avoid problems listed in Table 3.

There is no given optimum loading pattern which fits all or even most wastes for land treatment. The best policy is to load at the maximum rate which does not result in any of the problems mentioned in Table 3.

Oxygen

Adequate molecular oxygen is critical for efficient land treatment. Although anaerobic degradation occurs in soil, it must be limited for effective land treatment due to several reasons: (1) anaerobic biodegradation results in noxious products such as hydrogen sulfide, ammonia, amines and mercaptans; (2) anaerobic biodegradation is slower and less complete; and (3) in a reduced state, most hazardous metals are more water soluble.

Soil microorganisms use oxygen which has been transferred to soil water from the atmosphere. Thus, oxygen available for biodegradation is a function of: (1) amount of void space in the soil, (2) partial pressure of oxygen in the soil atmosphere, (3) oxygen transfer rate from soil atmosphere to soil water, (4) rate which soil microorganisms are using available oxygen, (5) geometric distribution of oxygen consuming soil area.

Oxygen is not rapidly transferred to water even under the best of circumstances, and active microbial metabolism can rapidly deplete it. As a rule of thumb, aerobic bacteria function well at ≥0.2 mg/l dissolved oxygen.

Overcash and Pal (1979) presented oxygen transfer rates for soils under given conditions (Table 4).

Oxygenation of soil is generally benefited by: (1) prevention of saturation with water; (2) presence of sand, loam (heavy clay undesirable for this criterion); (3) moderate tilling (over-tilling can produce opposite effect); (4) avoiding unnecessary compaction (heavy trucks, etc.); and (5) limited loading of rapidly biodegradable matter so that oxygen demand does not exceed oxygen transfer rate.

Available Water

The presence of water is essential for microbial activity, and nonspore forming microorganisms will eventually die at very low water concentrations. Although excessive water levels, per se, do not harm microorganisms, they quickly stifle aerobic metabolism.

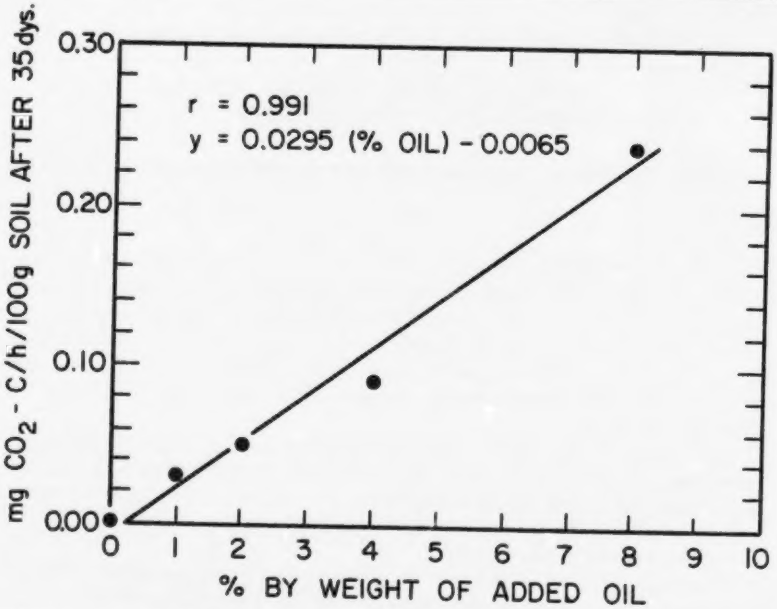

FIGURE 1. Regression of increase in soil respiration rate on oil addition to Malmo SiCl (10% organic matter) during incubation at 20° C with added fertilizer and control unoiled soil respiration subtracted (McGill 1980).

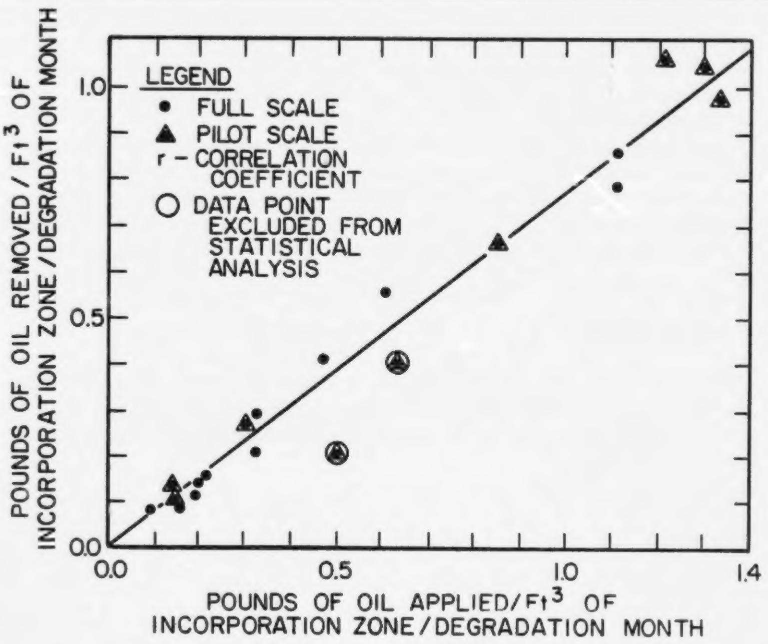

FIGURE 2. Oil removal rates as a function of oil application rates (API 1983).

As shown in Figure 3, the water content of soil typically ranges from 15 to 35 volume percent. At 35% most soils are water saturated. At the other extreme the concentration can drop lower than 15% under unusually arid conditions.

Soil water content is commonly addressed as percent of soil water holding capacity. A soil water holding capacity range of 25–100% is typically equivalent to a range of 7–28% volume percent. Moisture effect on respiration in the soil is illustrated in Figure 4.

Thus, there is little effect of moisture level over a wide range on biodegradation in the soil. As moisture drops below 25% of water holding capacity, the biodegradation rate can be expected to decline; at levels below 5%, lack of moisture may be lethal to soil microorganisms. The decline at higher water concentrations is due to reduced oxygen transfer.

The combined effect of moisture and temperature on biodegradation in the soil is reported to be more important than either factor alone (Smith 1982).

Temperature

Biodegradation declines with temperature due to reduced microbial growth and metabolic rates. The decline is nonlinear and biodegradation is essentially zero at the freezing point. Temperature effect is similar for mesophiles (grows best at moderate temperature, 25–40°C) and psychrophiles (capable of growth at 0°C), although the latter are relatively more active below 25°C than mesophiles (Smith 1982). Low temperature is not lethal to microorganisms, although repeated freezing and thawing will rupture some. In some instances land treatment will increase soil temperature due to increased metabolic activity and/or the presence of waste constituents. Added oil can result in soil being 1–10°C warmer (McGill 1980). High temperatures, well above those normally experienced in soil, cause very rapid decreases in growth and metabolism and become lethal. Psychrophiles begin to be adversely affected by higher temperature at about 30°C and mesophiles at about 40°C. Soil microbial activity is greatest between 20 and 37°C (Bossert and Bartha 1984).

Smith, citing Wildung et al., notes that in an arid soil less than 7% of observed variations in soil respiration rates could be attributed to temperature or moisture alone, but over 70% could be related to the two factors operating interactively. The author suggests the following correlations: (1) Sensitivity of biodegradation to moisture increases with temperature; (2) Sensitivity of biodegradation to temperature increases with moisture; (3) Sensitivity of biodegradation to temperature increases with decreasing temperature.

pH

The optimum pH for soil biodegradation lies between 6 and 8; however, effective biodegradation can be found outside this range. Microbial growth and metabolism are especially reduced by abrupt pH changes. In many land treatment operations soil pH is kept above pH 6 to avoid hazardous metal migration as well as to optimize microbial activity.

TABLE 3. Potential problems caused by overloading a land treatment system.

- Toxicity to degrading microorganisms
- Exceeding the soil binding capacity and resultant waste migration
- Oxygen starvation caused by demand exceeding transfer rate
- Water exclusion by hydrophobic components
- Creation of cultivation (mechanical problems)
- Waterlogging (oxygen starvation) if the waste has a high water content
- Crust or film formation on the soil surface

Presence of Other Nutrients

When waste is added to soil the presence or addition of a readily biodegradable carbon source may inhibit biodegradation of the waste (Bossert and Bartha 1984). Microorganisms tend to attack most readily available substrates, ignoring others until the ready supply is exhausted.

Wastes may lack required micronutrients for growth or biodegradation, but the soil will likely contain sufficient supplies. However, soils often contain insufficient amounts of available nitrogen (N) and phosphate (P) for efficient biodegradation of added waste. Availability of these nutrients for soil microbial growth is controlled by three factors: (1) Amount of N and P in the soil and rate at which they are mineralized (become available for use); (2) Amount of biodegradable carbon and available N,P in the added waste; (3) Rate at which the waste organic carbon is assimilated in the soil environment. By estimating or measuring these factors fertilization needs can be approximated.

Soil generally contains 5–12% organic matter (Overcash and Pal 1979), and of that, some 1–4% is mineralized annually (McGill 1980). Assuming that 5% of the organic matter is nitrogen and 0.5% is phosphate, some 50–480 lb/acre nitrogen (60–550 kg/hectare) and 5–48 lb/acre phosphorus (6–55 kg/ha) are available annually from soil for use by soil microflora to grow on waste added to the soil. Of course, high waste loading can quickly deplete these nutrients. McGill (1980), citing Rowell (1977), addressed such depletion pointing out that oil added to *poor* soil (low organic content) must be accompanied by fertilizer to achieve rapid oil biodegradation. Similarly he reported that fertilization of *rich* soil which received oil addition did not significantly enhance the rate of oil biodegradation. Routeau and Wildung (1970) suggest that a C/N ratio of <25 leads to mineralization (excessive N present) and a C/N ratio of >38 leads to depletion of mineralized N. The latter condition would limit biodegradation due to nitrogen starvation.

TABLE 4. Calculated oxygen transfer rates into various soils at 0.1. ATM water tension (Carlile and Phillips 1976).

Soil	Oxygen Transfer Rates $g/m^2/day$	 lb/a/day
Norfolk sl	82	732
Georgeville sil	64	571
Lakeland ls	96	857

(Adapted from Overcash and Pal 1979)

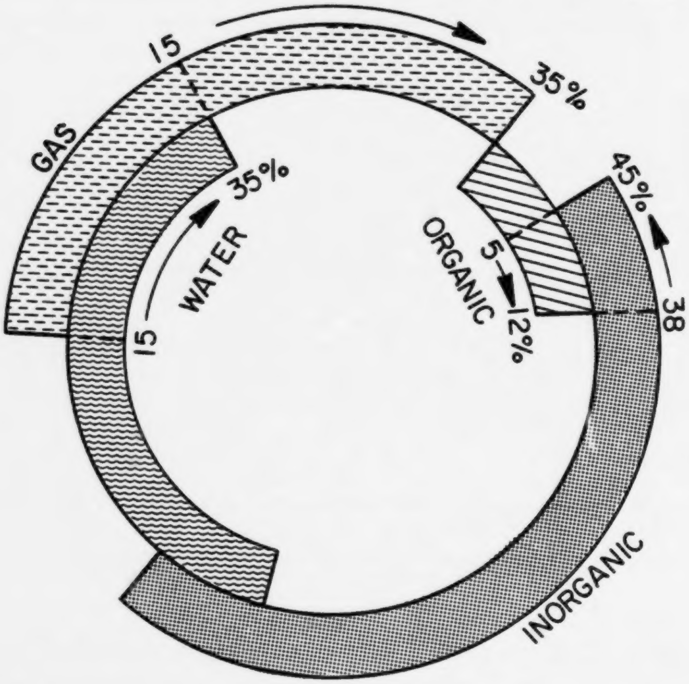

FIGURE 3. Typical volumetric composition of soil (adapted from Overcash and Pal 1979).

As a land treatment site matures, progressively less fertilization is required, because most of the nitrogen and phosphorus added to the site remains for reuse. McGill (1980) presented a model for estimating nitrogen fertilizer requirements for oil added to soil, and his summary (Figure 5) elegantly displays how land treatment fertilization schemes likely function. As he suggests, more field research is needed to confirm and quantify such interactions for various soils, climates and waste types.

Over fertilization can lead to groundwater or surface water problems while under fertilization leads only to slower than optimal biodegradation rates.

BIODEGRADATION RATES IN SOIL

Biodegradation rate is important in the land treatment process for two reasons: economics (the faster the rate, the less land required) and environmental safety (other factors equal, the faster the rate the less chance of environmenral problems due to presence of the waste).

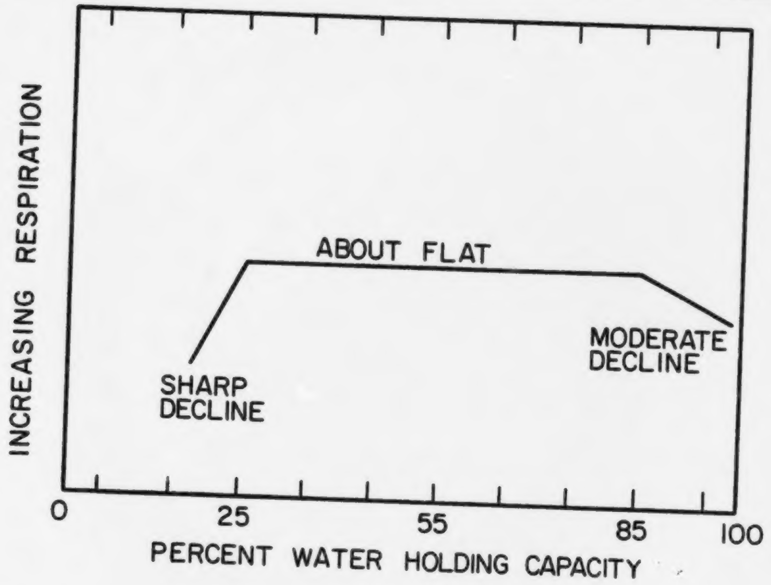

FIGURE 4. Effect of moisture on soil respiration (adapted from Smith 1982).

The relationship between biodegradation rate and migration has been emphasized by Overcash and Pal (1979) and by the API (1984). This relationship is critical for land treatment planning and operation.

While inherent and rapid waste biodegradability is desirable for land treatment, it is not necessarily essential. It is only necessary as it relates to environmental safety and economics. Rapidly degradable organics require more attention in terms of fertilizer and oxygen needs.

No attempt is made here to review all literature addressing biodegradation rates of waste constituents in soil. Rather, examples of substance classes which may be present in wastes are addressed. For many specific compounds not addressed here one can find helpful information in the literature. Furthermore, biodegradation rates are dramatically influenced by many variables, and caution must be exercised in comparing rate data from one set of studies to another. In spite of these limitations, we can usefully consider examples of biodegradation rates which have been reported for soil environments.

Organic Sulfur Compounds

Based on data presented by Overcash and Pal (1979) and credited to Frederick et al., organic sulfur compounds added at 10,000 ppm to soil degrade as follows:

	Biodegradation Rate (kg/wk)
Na-Taurocholate	950
Cystine	810
Formaldehyle Sodium Sulfoxide	620
Thiourea	85
Sulfanilamide	60
Sulfathiozol	50
Sulfapyridine	40
Mercaptoethanol	40
Na-Diethyldithiocarbamate	10

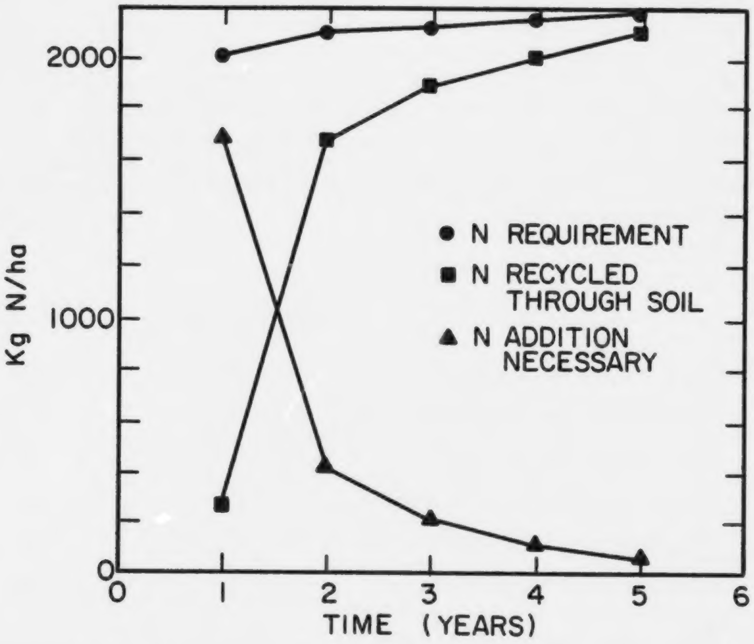

FIGURE 5. Trends in nitrogen requirements and supply during land farming for disposal of oily wastes (McGill 1980).

As pointed out by Overcash and Pal, these addition concentrations were very high and no chance for acclimation was given. Biodegradation of organic sulfur compounds may result in lower soil pH as a result of sulfur mineralization.

Phenols, Substituted Phenols

Overcash and Pal (1979) summarized reports dealing with biodegradation rates of phenols and substituted phenols in soil (Table 5). Many common soil and aquatic bacteria are capable of degrading such compounds; however, acclimation is important for high concentrations. Generally, biodegradation rates are slower for higher molecular weight and halogenated phenolics. Ring position of substitution also influences rate of biodegradation.

Synthetic Surfactants

At concentrations over 100 mg/kg in soil many surfactants adversely affect soil physical properties and may, at least temporarily, reduce microbial activity (Overcash and Pal 1979). Surfactant biodegradation in soil has not been extensively studied but available data indicate the importance of aerobic conditions and similar relative biodegradation patterns as found in aqueous environments where there has been extensive study (Straus 1963; Robeck et al. 1964; Overcash and Pal 1979; Swisher 1970; Gledhill 1974; Cain 1981; Huddleston and Allred 1967).

Surfactant biodegradation rates and extents are strongly related to molecular structure. Highly branched compounds are especially resistant and some quaternary ammonium compounds may be so tightly bound to clays that biodegradation is difficult. Relative biodegradation rates and extents for principal classes of synthetic surfactants are:

	Relative Rate	Extent (%)
Linear Alcohol Sulfates	100	100
Linear Alkylbenzene Sulfanates (LAS)	75	100
Linear Alcohol Ethoxylates	70	100
Quaternary Ammonium Compounds*	60	100
Alkyl (branched) Phenol Etholxylates	10	100
Alkyl (branched) Benzene Sulfonates	5	50

*Certain structures are more bioresistant.

TABLE 5. Rates of degradation of phenol and substituted phenols (Overcash and Pal 1979).

Compound	Applic. Rate	Degradation Rate	Reference
Pyrocatechin	500 mg/kg	100% in 1 day	Medvedev and Davidov 1972
Hydroquinone	500 mg/kg	100% in 1 day	" " "
Resorcinol	"	100% in 2 days	" " "
Phenol	"	100% in 2 days	" " "
Phenol	"	100% in 6 days	Alexander and Aleem 1961
Thymol	"	100% in 3 days	Medvedev and Davidov 1972
2,4-Xylenol	"	100% in 4 days	" " "
αNaphthol	"	100% in 5 days	" " "
p-Cresol	"	100% in 7 days	" " "
p-hydroxybenzoic acid	"	100% in 7 days	Haider and Martin 1976
O-Cresol	"	100% in 8 days	Medvedev and Davidov 1972
3,4-Xylenol	"	100% in 9 days	" " "
1,4-Naphthoquinone	"	100% in 9 days	" " "
m-Cresol	"	100% in 11 days	" " "
3,5-Xylinol	"	100% in 11 days	" " "
2,5-Xylinol	"	100% in 14 days	" " "
B-Naphthol	"	Very little in 90 days	" " "
Pentachlorophenol	100 mg/kg	1/2 life of 40 days	Kuwatsuka 1972
Various mono, di, and tri hologenated phenols		Ring cleavage in 2-4 weeks	Alexander 1972

In water, linear alcohol sulfates are completely degraded within 24 hours and LAS within 3–4 days.

Hydrocarbons

Perry and Cerniglia, cited by Overcash and Pal (1979), reported relative biodegradability of hydrocarbons to be:

More Difficult to Degrade ↓

Linear Alkanes C_{10-19}
Linear Alkanes C_{12-18}
Gases C_{2-4}
Alkanes C_{5-9}
Branched Alkanes C_{12}
Alkenes C_{3-11}
Branched Alkenes
Aromatics
Cycloalkanes

Ryan et al. (see API 1984) summarized degradation rates of two environmentally important hydrocarbons (both aromatics) in the soil.

Compound	Initial Concentration	1/2 Life (Days)	Reference Cited
Toluene	5,000-10,000 mg/kg	0.7-1.7	Donnelly 1979
Toluene	-	7	Berkowitz et al. 1981
Naphthalene	7	0.12	Herbes & Schwall 1978
Naphthalene	7	125*	Herbes & Schwall 1978
Naphthalene	7	4**	Herbes & Schwall 1978

* <15°C
** >25°C

Miscellaneous Organic Compounds, Materials

In their review of organic materials biodegradation in the soil, Overcash and Pal (1979) presented the data shown in Table 6.

TABLE 6. Biodegradation rate for miscellaneous organic compounds in soil (Overcash and Pal 1979).

Compound	Test Conc.	Biodegn (or Loss) Rate	Reference Cited
Aniline	500 ppm	100% in 13 days	Medvedev and Davidov 1972
p-toluidine	"	100% in 9 days	" " "
o-toluidine	"	100% in 3 days	" " "
2,4-dimethylaniline	"	100% in 2 days	" " "
2,6-dimethylaniline	"	100% in 3 days	" " "
acetic acid[1]	1000 ppm	52-76% in 7 days[2]	Martin and Haider 1976
	"	71-87% in 84 days[3]	" " "
	"	50% in 5 days[2]	Sorenson and Paul 1981
	"	80% in 80 days[3]	" " "
pyruvic acid[1]	"	47-83% in 7 days[2]	Martin and Haider 1976
	"	70-93% in 84 days[3]	" " "
succinic acid[1]	"	52-89% in 7 days[2]	" " "
	"	71-95% in 84 days[3]	" " "
glucose[1]	"	75% in 7 days[2]	" " "
	"	87% in 84 days[3]	" " "

[1] Mineralization data

[2] Range found for compound radiolabeled in different position than for companion study (footnote 3)

[3] See explanation for footnote 2

Phthalic Acid, Phthalate Esters

Inman et al. (1984) reported on biodegradation of phthalic acid, monobutyl phthalate, and dibutyl phthalate in soil using ^{14}C radiolabeled substrates to monitor complete decomposition. Degradation of the esters followed 10–20 days of lag time while phthalic acid was attacked immediately.

Compound	Conc. Added	Approx. Time Required--Complete Biodegn
Phthalic Acid	1000 ppm	50 days
Monobutyl Phthalate	1000 ppm	155 days
Dubutyl Phthalate	1000 ppm	186 days

Polynuclear Aromatic Hydrocarbons (PNA)

Biodegradation of polynuclear aromatic hydrocarbons (PNA's) was recently reviewed by Cerniglia (1984) and much of the following information is from that source. Microbial metabolism of PNA's has largely been studied using pure cultures and single-compound, laboratory-scale systems. There are few reports of PNA biodegradation under field conditions and very few dealing with soil systems specifically.

A wide range of soil organisms including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae have been shown to have the enzymatic capacity to oxidize several PNA's. Prokaryotic organisms, bacteria, and cyanobacteria, use different biodegradation pathways than the eukaryotes, fungi, and algae, but both involve molecular oxygen.

The bacterial oxidation pathway of terminal ring cleavage appears to apply to all PNA compounds. Biodegradability and water solubility appear to be inversely related to the number of rings in the molecules.

In a laboratory simulation of land treatment Bossert et al. (1984) found a PNA decrease of 3.3 μg/g of soil per day over a two-year "active" period of waste addition. During a subsequent one-year "closure" period the PNA decrease was 0.1 μg/g soil per day. However, nearly half the loss appeared to be due to abiotic mechanisms.

They examined three- to six-ring compounds and found extensive degradation (to 99%) of three-ring and some four-ring PNA's. The condensed four-ring compounds were relatively recalcitrant and all the five- and six-ring PNA's resisted degradation (from 0 to 70% loss).

Sims (1982) found half-lives of 11 PNA's to be 18–190 days when added to soil at 1 to 147 ppm. He concluded that initial concentration had no effect on degradation rate over the addition range studied.

Oil and Grease

Land treatment of biodegradable waste oils and greases is attractive strategy because they tend to be tightly bound to soil, offering large surface areas for degradation. Accordingly, a large amount of soil biodegradation data for oils and greases has been reported (see Table 7). Full-scale operations are addressed in the next section of this presentation.

Data in Table 7 should not be closely compared because significant environmental differences undoubtedly existed across the studies presented. Nevertheless, petroleum biodegradation rate in soil appears to be similar to that for vegetable oils and is attractive over a wide range of climate.

TABLE 7. Reported oil & grease biodegradation rates in soil. (continued on p. 58)

Type - Location	Rate (Oil) g/kg Soil/yr	Rate (Oil) lb/ft^3 Soil/yr	Reference
Petroleum			
Crude Oil - Tx, Ok, Pa, Avg.	15	1.3	Raymond et al. 1975
Crude Oil - Oklahoma	10	0.9	Huddleston et al. 1984
Crude Oil - Canada	55-237[4]	4.9-20.9	Toogood 1977[2]
Crude Oil (Paraffins) Ok	3	0.3	Huddleston et al. 1984
Crude Oil (Aromatics) Ok	3.5	0.3	Huddleston et al. 1984
Crude Oil (Asphaltics) Ok	4	0.4	Huddleston et al. 1984
Raffinate - Texas	139	10.9	Kincannon 1972[1]
Heating Oil - Tx, Ok, Pa, Avg.	13	1.1	Raymond et al. 1975
#6 Fuel Oil - Tx, Ok, Pa, Avg	16	1.4	Raymond et al. 1975
#6 Fuel Oil - Texas	97	12.8	Kincannon 1972[1]
Refinery Waste - Texas	69	6.2	Kincannon 1972[1]
Refinery Waste - Oklahoma	12.5	1.1	Huddleston and Meyers 1980[3]
Refinery Waste - Oklahoma	75	6.6	Weldon 1980[3]
Refinery Waste - Oklahoma	28	4.5	Weldon 1980[3]
Refinery Waste - Oklahoma	12	2.7	Weldon 1980[3]
Refinery Waste - Texas	14	1.2	Weldon 1980[3]
Refinery Waste - Texas	11	1.0	Weldon 1980[3]
Refinery Waste - Texas	29	2.5	Weldon 1980[3]
Refinery Waste - Ohio	8	3.1	Weldon 1980[3]
Refinery Waste - Ohio	10	3.2	Weldon 1980[3]
Refy Waste (Paraffin) Ok	184	16.2	Meyers and Huddleston 1979

TABLE 7. Continued.

Type - Location	Rate (Oil) g/kg Soil/yr	Rate (Oil) lb/ft[3] Soil/yr	Reference
Refy Waste (Aromatics) Ok	49	4.3	Meyers and Huddleston 1979
Refy Waste (Asphaltenes) Ok	37	3.2	Meyers and Huddleston 1979
Tank Sludge - Canada	16	1.5	Norris 1968[2]
Tank Sludge - Texas	24	7.6	Kincannon 1972[1]
Oil Wastes - Tennessee	171	15.0	Franke and Clark 1974[1]
Lube Oil Waste - Tennessee	171	15.0	Franke and Clark 1974[1]
Lube Oil Waste - Tx, Ok, Pa, Avg.	18	1.6	Raymond et al. 1975
Lube Oil Waste - New Zealand	17-454	2.3-40	Huddleston 1979
Mineral Oil	38-77	3.3-6.8	Overcash and Pal 1979
Vegetable Oil			
Palm Oil	14-91	1.8-8.0	Overcash and Pal 1979
Soybean Oil	17-96	1.5-8.5	Overcash and Pal 1979
Waste Cooking Oil	59-190	5.2-16.8	Overcash and Pal 1979

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[1] Overcash and Pal 1979
[2] PACE 1981
[3] API 1983
[4] Range - Low to High Loading Rate

BIODEGRADATION RATES IN FULL-SCALE LAND TREATMENT SYSTEMS

There are few definitive data in the literature quantifying waste biodegradation rate in full-scale land treatment systems. This is rather surprising in view of the industrial interest in land treatment indicated by Overcash and Pal (1979).

Rate data which could be found are given in Table 8 and are almost all oil industry reports. The API (1983) examined rates with respect to "degradation months" which were defined as months having an average air temperature above 50°F. This narrowed reported oil degradation values from 0.57–10.28 lb/ft^3/mo to 0.09–0.86 lb/ft^3/mo.

Clearly more quantitative operational biodegradation information is needed to usefully relate laboratory and pilot findings to full-scale land treatment.

TABLE 8. Biodegradation rates reported from full-scale land treatment operations.

Waste	Location	Loading		Degradation Rate		Reference
		g/kg soil/yr	lb/ft^3 soil/yr	g/kg soil/yr	lb/ft^3 soil/yr	
Refinery Oily Waste	Montana	11	0.98	6	0.57	API 1983
	California	148	12.25	114	10.28	API 1983
	New Jersey	87	7.82	61	5.47	API 1983
	Illinois	16	1.40	11	0.98	API 1983
	Louisiana	44	4.00	39	3.52	API 1983
	Washington	22	1.97	14	1.26	API 1983
	Texas	29	1.97	22	1.96	API 1983
	Texas	79	7.16	75	6.73	API 1983
	Texas	62	5.62	55	4.94	API 1983
	Oklahoma	67	6.00	53	4.80	API 1983
	Oklahoma	17	1.54	11	0.98	API 1983
	Texas	-	-	165	15	Kincannon 1972[1]
Heavy Oil	Oklahoma	1.2	0.11	0.5	0.05	Huddleston et al. 1984
Sulfite Liquor Wastes		<150 lb BOD_5/acre/day		100%		Wallace 1976 (see Loehr et al. 1979)
Vegetable Canning Wastes		1300 lb COD/acre/day		99%		Jewell and Loehr 1975 (see Loehr et al. 1979)
Potato Processing Wastewater		10-85 T COD/ha/yr		>80%		Smith et al. 1977

[1] Huddleston 1979

SUMMARY

The biodegradation function of the land treatment process is a unique and valuable resource for managing many wastes in an environmentally safe, efficient and economic fashion. However, as evidenced by this presentation, there is a paucity of definitive, quantitative data describing biodegradation rates and extents for waste constituents in full-scale field land treatment operations. Such data is essential for suitable, predictive land treatment planning and utilization of the process to its maximum potential. It is up to us who use land treatment to generate such data.

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ABIOTIC PROCESSES AFFECTING THE TRANSPORT OF ORGANIC POLLUTANTS IN SOIL

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ABSTRACT

The efficiency of hazardous waste land treatment (HWLT) is determined by a number of soil and waste properties and the waste management practices employed. The total amount of waste organic constituents (WOCs) leaching past the treatment zone, defined here as the *mass emission*, may be used as an index of the efficiency of HWLT. Mass emission is determined by (a) partitioning, (b) travel time, and (c) persistence of the WOCs within the treatment zone. Sorption of WOCs, i.e., distribution between soil and pore fluid, is a key process that influences the travel time and the rate at which various attenuating processes can occur in the treatment zone. In this paper, factors influencing sorption and leaching of WOCs in soils are reviewed, with emphasis on sorption from complex mixtures consisting of mixed solvents and multiple sorbates. Presence of water-miscible organic cosolvents can drastically decrease the sorption of WOCs, which enhances their leaching. Available data suggest that nonpolar WOCs may sorb independently from a waste mixture, but competitive sorption effects must be considered for ionic or ionizable WOCs.

INTRODUCTION

The disposal of hazardous chemical wastes has become the topic of environmental interest and concern both to lay public and scientists. Subtitle C of the Resource Conservation and Recovery Act (RCRA) creates a "cradle-to-grave" management system to ensure that hazardous wastes are safely treated, stored, and disposed. Among the disposal techniques being considered, land disposal (i.e., surface impoundments, landfills, etc.) and land treatment have received considerable attention in recent years. The former techniques of waste management are based on containment or isolation of the waste within a treated area by

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the use of liners and surface seals and by requiring waste leachate and runoff minimization, collection, and treatment.

Hazardous Waste Land Treatment (HWLT), on the other hand, involves application of the waste materials to the surface soil layers in order to immobilize, transform, or degrade the waste organic constituents (WOCs) within the treatment zone, such that the leachate leaving this zone meets certain preset environmental safety and health standards. The land treatment technique offers the advantage that for liquid wastes, the total volume can be greatly reduced.

Because HWLT depends solely on various physical, chemical, and biotic processes that attenuate the WOCs, a complete understanding of these processes is essential for successful design and operation of a HWLT site. In order to predict the extent of waste attenuation achieved within the treatment zone, it is necessary that the partitioning, travel time, and persistence of the WOCs in this zone be described. *Partitioning* refers to the distribution of the WOCs among the different phases (soil, liquid, gas, and biota). The total amount of time a WOC resides within the treatment zone is referred to here as the *travel time*. The *persistence* of a WOC within the treatment zone is determined by various biotic and abiotic processes that lead to degradation and/or detoxification of the chemical. Attenuation of a WOC is measured in terms of the fraction of surface-applied chemical that leaches past the treatment zone; this amount is defined as the *mass emission*. Attenuation defined in this manner does not include dilution of the WOC. The goal of HWLT is to maximize pollutant attenuation by minimizing mass emission.

The travel time directly influences the extent to which a WOC may be attenuated, since it is the total time available for various attenuating processes to act on the chemical. The travel time is dependent upon a large number of physical-chemical properties of the waste and of the soil at the site as well as the waste management practices (e.g., frequency and loading). A detailed discussion of all these factors is beyond the scope of this paper. Instead, we will focus our attenuation on sorption of WOCs by soil, a process that determines the travel time and the rate at which many of the biotic and abiotic transformation processes occur in the treatment zone.

Sorption From Single Solute Systems

Sorption is defined as the partitioning of the WOCs between soil and the pore fluid. A number of review articles have dealt with organic pollutant sorption on soils and sediments (Hamaker and Thompson 1972; Rao and Davidson 1980; Karickhoff 1981, 1984; Lyman et al. 1982). These papers have summarized published data on sorption and evaluated various methods for predicting sorption of organic pollutants from aqueous solutions.

WOC sorption on soils can be described by the Freundlich equation,

$$S = K\,C^{N} \tag{1}$$

where S is the sorbed concentration (mg WOC/kg soil), C is the solution concentration (mg WOC/liter solution), and K and N are sorption coefficients whose values are unique to each WOC-soil-solvent combination. The N value in Eq. (1) is a measure of the linearity of the sorption isotherm. The N value varies between 0.6 and 1.0 for pesticide sorption on soils (Hamaker and Thompson 1972; Rao and Davidson 1980) and is equal to 1.0 for sorption of a number of nonpolar organic pollutants (Chiou et al. 1979, 1983; Swarzenbach and Westall 1981; Karickhoff et al. 1979; Karickhoff 1981, 1984). When $N = 1$, Eq. (1) simplifies to a linear isotherm, $S = K_D C$.

The value of the sorption coefficient (K or K_D) is a measure of the WOC's preference to be in the sorbed state. A considerable amount of research conducted over the past two decades suggests that the K value for nonpolar WOCs is determined primarily by three factors: (a) the amount of the nonpolar or lipophilic surface available on the sorbent (soil), (b) lipophilicity of the solute (WOC), and (c) surface tension of the solvent (usually water) from which sorption takes place.

The soil organic carbon content (OC) is an excellent measure of the amount of the lipophilic surface area available for sorption. Thus, a close relationship is noted between K (or K_D) values for a large number of nonpolar organic pollutants and OC (e.g., Hamaker and Thompson 1972; Rao and Davidson 1980; Karickhoff 1981). This has led to the calculation of a soil carbon-normalized sorption coefficient, $P = K/OC$ or $P = K_D/OC$. For a given organic pollutant, the P value may vary only within a factor of two for a number soils and sediments as well as for various size fractions isolated from a given soil or sediment.

Various indices of solute lipophilicity have been investigated. Among these, aqueous solubility (S, mg/L; X_w, mole-fraction), octanol-water partition coefficient (K_{ow}), and nonpolar molecular surface area (HSA, nm^2) have been correlated with P values. Since decreasing aqueous solubility is an indication of increasing lipophilicity, inverse relationships have been found been S (or X_w) and P (Karickhoff 1981, 1984). Since octanol is a lipophilic solvent (and assumed to represent lipophilic soil organic matter), larger K_{ow} values suggest increasing solute lipophilicity. Hence, P and K_{ow} are directly related (Karickhoff et al. 1979; Karickhoff 1981, 1984). Larger values of HSA represent increasing solute lipophilicity and log-linear relationships between P and HSA have been reported (Dzombak and Luthy 1984; Rao et al. 1985a).

In dissolving a nonpolar solute, a "cavity" has to be created in the solvent. With increasing solvent surface tension (Y) and/or the solute size (i.e., HSA), the energy required to create the cavity also increases. For a given solute, solubility is greater in solvents with a smaller Y. Thus, addition of salts increases the surface tension of water and lead to decreased solubility and increased sorption; this effect is commonly referred to as "salting out." If water-miscible organic solvents (e.g., methanol, ethanol, acetone, etc.) are added to water, the surface tension of the mixed solvent decreases, which in turn leads to an increased solubility and a decrease in sorption.

The sorption of organic pollutants from mixed solvents has been explored by Rao et al. (1985a). They showed that for sorption from a binary solvent,

$$\ln (P^m / P^w) = - \alpha \sigma f^c \tag{2}$$

where P is the soil carbon-normalized sorption coefficient with the superscripts m and w representing mixed solvent and water, respectively; f^c is the volume-fraction of the organic cosolvent, α is an empirical constant; and the σ value is unique to a solvent-solute combination. The σ value is directly proportional to solvent surface tension (Y) and solute HSA (Rao et al. 1985a). With increasing f^c, the relative sorption coefficient (P^m/P^w) decreases log-linearly. Nkedi-Kizza et al. (1985a) have successfully tested the validity of Eq. (2) with batch sorption data.

The implication of Eq. (2) to HWLT should be evident since the pore fluid might very well consist of a mixture of organic solvents and water. Thus, a direct extrapolation of data based on aqueous solutions to predict WOC sorption on soils at a HWLT site is not advisable. The effects of organic cosolvents, if present, should be considered as shown above. Rao et al. (1985a) and Woodburn et al. (1985) discuss the extension of Eq. (2) for sorption from mixed solvents comprising of multiple organic solvents.

Sorption from Multi-Solute Systems

The foregoing discussion has focused on organic pollutant sorption from aqueous and mixed solvents containing a single pollutant. Since complex wastes consisting of various pollutants are disposed at a HWLT site, the data and sorption models based on single-solute systems need to be extended for multi-solute complex mixtures. Though this aspect has been extensively investigated for sorption of trace organics on activated carbon, only recently have investigations been conducted using soils or sediments as the sorbents. Swarzenbach and Westall (1981), Karickhoff et al. (1979), and MacIntyre and deFur (1985) have reported that nonpolar organic pollutants are sorbed independently on soils or sediments or clays. Similar results have also been reported by Nkedi-Kizza et al. (1985b) for sorption of toluene and naphthalene as well as for three pesticides. Their data are reproduced in Figures 1 and 2. The sorption isotherms measured in single-sorbate and ternary-sorbate systems are identical, suggesting noncompetitive sorption of these solutes by the Eustis soil (a fine sand with 0.6% OC, 94% sand, and 3% each of silt and clay).

For ionizable organic compounds (such as various phenols, catechols, and amines) that are likely to be encountered at a HWLT site, the problem of predicting sorption from single- or multiple-sorbate mixtures is somewhat more complicated. Available data suggest that the ionic status of the soil and the solute must be considered in deciding whether competitive sorption occurs. The ionic charge on the soil is determined by the soil pH and the zero point of charge (ZPC), while the ionic status of the solute is determined by the solution pH and its pK_a. Boyd (1980) and Zachara (1984) have examined such effects. Nkedi-Kizza et al. (1985c) present data for sorption of substituted phenols from complex mixtures. Brown and Combs (1984) evaluated a competitive Langmuir sorption model using sorption data for methylacridinium (a cationic molecule).

Leaching of WOCs in Soil

As indicated earlier, one of the major factors that determines the efficiency of HWLT is the total travel time (t_r) for WOCs within the treatment zone. The t_r

value for a given WOC is a complex function of site and waste properties and the site management. Given site-specific information, comprehensive simulation models may be developed to predict the actual travel time for each of the WOCs. Rao and Jessup (1982, 1983), among others, have discussed various simulation models and their practical limitations in predicting sorption and leaching of organic pollutants in soils under field conditions.

As an alternate to comprehensive simulation models, it may be feasible to use simple indices for ranking the WOCs in terms of *relative rates of leaching* within the treatment zone. Such an approach can be developed (Jury et al. 1983; Rao et al. 1985b) on the basis of the solute leaching retardation factor (R):

$$R = [\,1 + \frac{\delta(OC)P^{w}}{\theta}\,] \tag{3}$$

where δ is the soil bulk density in terms of megagrams per cubic meter (Mg/m3), θ is the volumetric soil-water content (m^3/m^3), OC is fractional soil organic content, and P^w is the sorption coefficient (m^3/Mg). In the presence of binary solvents, Eq. (3) should be modified as follows (Rao et al. 1985a):

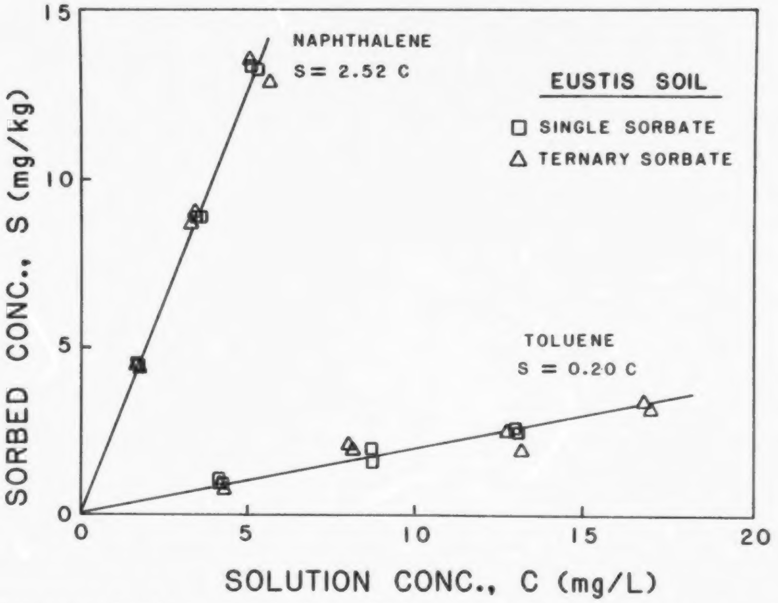

FIGURE 1. Isotherms for sorption of toluene and naphthalene by Eustis soil from single sorbate and ternary sorbate systems (benzene, toluene, and naphthalene) (Nkedi-Kizza et al. 1985b).

$$R = [1 + \frac{\underset{e}{\delta(OC)P^{W}\exp(-\alpha\,\sigma\, f^{c})}}{\theta}] \tag{4}$$

where the parameters α, σ and f^{c} are as defined in Eq. (2), and the parameters δ, OC, θ, and P^{w} are as defined in Eq. (3). For $f^{c} = 0$ (i.e., aqueous systems), Eq. (4) simplifies to Eq. (3).

The retardation factor (R) may be simply interpreted as a *relative velocity* and computed as the ratio of the velocities of water (or a nonadsorbed chemical) and an adsorbed chemical (v_w and v_i, respectively). Thus,

$$R = (V_w / V_i) \tag{5}$$

Note that $1.0 \leq R \leq \infty$. For a nonadsorbed chemical (i.e., $P^{w} = 0$), $R \equiv 1$, and the WOC rate of leaching is identical to that of water. As the value increases, the retardation of WOC leaching increases (i.e., $R > 1$ and $v_i < v_w$). It is evident then that a ranking of the WOCs in ascending order of R values will in fact yield a ranking in terms of their travel times through the treatment zone. This procedure

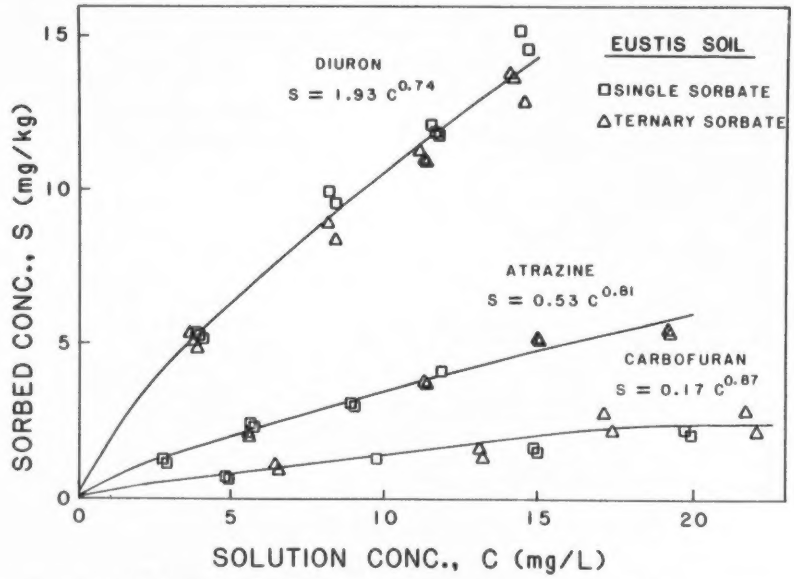

FIGURE 2. Isotherms for sorption of three pesticides on Eustis soil from single sorbate and ternary sorbate systems (atrazine, carbofuran, and diuron) (Nkedi-Kizza et al. 1985b).

has been used by Jury et al. (1983) and Rao et al. (1985b) to screen pesticides for evaluating their potential to contaminate groundwater. The R value factors may also be used to select the "Potential Hazardous Constituents" (PHCs) in a waste designated for land treatment (Rao et al. 1985c).

From Eq. (4), the retardation of solute leaching decreases exponentially with increasing amount of an organic cosolvent in a binary solvent. The parameter σ in Eq. (4) is a measure of how significant the cosolvent effect will be. Figure 3,

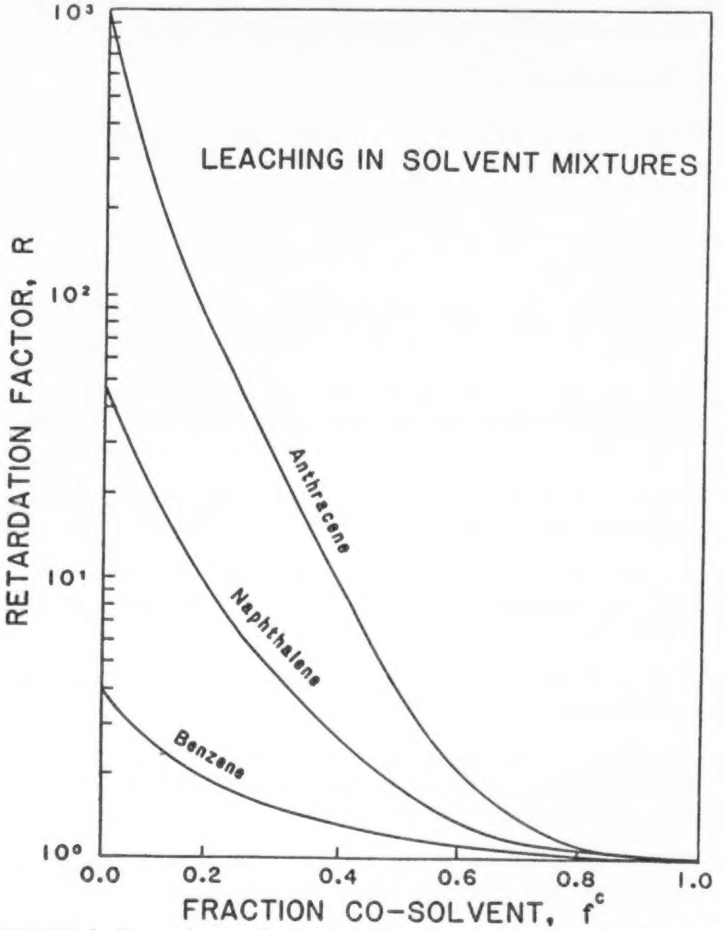

FIGURE 3. Dependence of solute leaching retardation factor (R) on the volume fraction of organic cosolvent in a binary solvent mixture (Rao et al. 1985a).

taken from Rao et al. (1985a), graphically illustrates the dependence of R on f^c for several organic pollutants. Nkedi-Kizza et al. (1985d) presented experimental data for leaching of two pesticides through soil columns with binary solvents (methanol-water to illustrate this effect. They reported that for soil columns eluted with 50% methanol ($f^c = 0.5$), the herbicides atrazine and diuron leached at the same rate as tritiated water, which was used as a nonadsorbed tracer of water. Thus, it is essential that the impact of organic cosolvents on WOC leaching at a HWLT site be recognized. In the presence of organic cosolvents, the travel times for WOCs may be considerably smaller and consequently their attenuation within the treatment zone will decrease.

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ACCUMULATION OF ORGANIC WASTE CONSTITUENTS IN TERRESTRIAL BIOTA[1,2]

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INTRODUCTION

The accumulation of hazardous organic chemicals by terrestrial plants and animals has received greater consideration with the passing of the amendments to the Resource Conservation and Recovery Act (RCRA) in November of 1984. As amended, RCRA states in part that:

> . . . the administrator shall . . . develop and promulgate criteria for identifying the characteristics of hazardous waste . . . taking into account toxicity, persistence, and degradability in nature, *potential for accumulation in tissue*, and other related factors such as flammability, corrosiveness, and other hazardous characteristics. [SUBTITLE C, SEC. 3001.(a)] [italics added].

Thus, chemical accumulation in biota, or bioaccumulation, has become one of the parameters by which wastes are to be judged in order to establish their suitability for land treatment. For the most part, the major organic constituents of wastes acceptable for land treatment are likely to be readily degradable substances of which living tissues are also made. These substances can be utilized for energy by microorganisms or other soil biota and rarely pose a hazard. Many of the wastes from agriculture, food processing, and municipal sewage may also contain cellulose, lignins, waxes or other substances (Stewart and Webber 1976) that are degraded slowly but are relatively inert and rarely of toxicological concern. On the other hand, many xenobiotics (exogeneously derived substances of no nutritive value to organisms, especially synthetic organic chemicals) can become problematic because of their propensity to accumulate in biota. Such substances are likely to be encountered in land treated wastes not as major components but as trace constituents with the potential to become harmful only after prolonged exposure of plants or animals. Because few data exist on the movement of organic waste constituents into plants and animals during land treatment, examples of this phenomena come from situations other than land treatment, especially that of insecticide use in agriculture. In this review, key papers are summarized that contribute to generalizations about the characteristics of organisms and specific xenobiotics influencing bioaccumulation. The processes of biological degradation and transport of organic chemicals in soils, both of which can affect bioaccumulation, are reviewed elsewhere in these proceedings.

BIOACCUMULATION—IMPLICATIONS FOR FATE AND EFFECTS OF XENOBIOTICS

Bioaccumulation is unlike most environmental processes affecting contaminants in that it reflects enrichment in the concentration of a chemical rather than diminution or dissipation. It is usually expressed as a bioconcentration factor (BCF),

$$\mathrm{BCF} = \frac{[\text{chemical}]_{\text{organism or tissue}}}{[\text{chemical}]_{\text{soil or water}}} ,$$

that is, the ratio of the chemical concentration in an organism or its tissues at equilibrium relative to the ambient concentration, usually that of soil or water. Thus, BCFs greater than one show enrichment, which is sometimes referred to as biological magnification.

It is important to realize that bioaccumulation per se does not necessarily pose a hazard to human or environmental health. In fact, the ability of an organism to remove a toxicant from circulation in body fluids and to sequester it in some tissue compartment, e.g., fat, can be a survival advantage (Loomis 1978). Yet, bioaccumulation can also lead to adverse effects when it serves as a mechanism for xenobiotic exposure of higher trophic levels, either wildlife or human, or as the cause of chronic or acute toxic effects. The latter are most likely to occur when an organism is under stress and utilizes fat reserves, for example, during illness, starvation, or migration. Resulting sublethal effects may be subtle—a decrease in fertility, a lowering of disease resistance, behavioral or mood changes, impaired intellectual performance are among the possibilities (Sheehan 1984). Dispersal of xenobiotics from a site may also occur as a consequence of bioaccumulation, as when crops are grown on a contaminated site and harvested. Chemical dispersal from the site of contamination as a consequence of bioaccumulation is more likely to be significant for plants, due to their greater biomass in ecosystems, than for animals.

The RCRA requirement of addressing bioaccumulation poses a problem because standardized experimental methods have not been established to evaluate accumulation of toxicants by terrestrial organisms in natural systems. Much more is known about uptake of inorganics such as arsenic, cadmium, and lead than is known about organic contaminants (Allaway 1977; Baxter et al. 1983; Chaney 1980, 1983; Hansen and Chaney 1984). Yet, organics are the most promising types of compounds for land disposal because of the possibility, unlike inorganics, for complete catabolism and detoxication due to mineralization and degradation processes.

Aquatic toxicologists are much more advanced than their terrestrial counterparts in methodology, both experimental and theoretical, for measuring and modeling contaminant movement into biota (e.g., Spacie and Hamelink 1982, 1985). Unfortunately, these methods are not appropriate for bioaccumulation of land treated wastes, primarily because factors governing uptake in aquatic systems differ from those in terrestrial systems. For example, movement of xenobiotics across the gills is the major pathway for uptake of most contaminants in fish (Southworth et al. 1982) and food contributes relatively little (Kay 1984), whereas ingestion is the predominant route of entry in terrestrial animals (Moriarty 1983). Water solubility can become a limiting factor for xenobiotic exposure in aquatic systems, especially because chemicals that are accumulated are usually hydrophobic. Conversely, terrestrial animals are often exposed to xenobiotics in concentrations far in excess of those that would saturate water. Thus, BCFs for lipophilic, persistent organics are commonly measured at 10^3 to 10^5 for aquatic biota but rarely reach 10^2 for terrestrial organisms, even though maximum xenobiotic residues are the same order of magnitude in tissues for both aquatic and terrestrial organisms (Kenaga 1972).

PREDICTING BIOACCUMULATION

An important question to be asked about bioaccumulation and land treatment is whether accumulation of organic waste constituents in terrestrial animals can be predicted, once a waste has been chemically characterized. Kenaga (1980) suggested that tissue concentrations of chemicals in fish might be used to predict tissue concentrations of the same substances in cattle and swine. Indeed, the ability to use fish accumulation data for predicting zenobiotic accumulation in terrestrial fauna would be quite useful. However, a more recent study reviewing a larger set of published data is less optimistic. Garten and Trabalka (1983) found that bioaccumulation in fish and vertebrates were poorly correlated (Table 1). In separate regressions of contaminant concentrations in ruminant fat, nonruminant fat, and avian fat versus concentrations of the corresponding contaminants in fish, correlation coefficients of determination (r^2) were 0.59, 0.09, and 0.20, respectively. These findings support the continued use of feeding tests with rodents for predicting bioaccumulation in larger animals and birds rather than attempting to extrapolate to vertebrate species from data obtained for fish.

A number of physicochemical properties of molecules have been used to predict BCFs of organic chemicals in aquatic organisms. The partition coefficient (K_{ow}) for chemicals in a biphasic system of n-octanol and water is the most extensively used physicochemical parameter for predicting BCFs in aquatic organisms. Commonly used methods for estimating BCFs based on partition coefficients are summarized by Bysshe (1982). As part of a study to assess the usefulness of the partition coefficient as a predictor of bioaccumulation, Garten and Trabalka (1983) compiled data on xenobiotic accumulation in body lipids of terrestrial vertebrates. A total of 122 observations were found for 68 chemicals. In a tabulation of these data as a function of partition coefficient ($\log K_{ow} \pm 0.5$) and bioconcentration factor ($\log BCF \pm 0.5$), certain patterns became evident (Table 2).

TABLE 1. Linear regression of bioaccumulation factors in ruminant fat, nonruminant fat, and bird fat with bioaccumulation factors for fish based on an extensive literature review (Garten and Trabalka 1983).

Variables (log)				
x	y	N[a]	Regression equation	r^2[b]
Ruminant fat	Fish	23	$y = -3.839 + 0.869x$	0.59
Nonruminant fat	Fish	31	$y = -1.147 + 0.311x$	0.09
Avian fat	Fish	24	$y = -1.180 + 0.464x$	0.20

[a] N = number of observations.

[b] r^2 = coefficient of determination.

Chemicals that were enriched in animal fat (BCF > -0.5) all had partition coefficients of 3200 or greater (log $K_{ow} \geq 3.5$). Conversely, none of the chemicals with log K_{ow} less than 3.5 were found to bioaccumulate. The observations that fell in the upper right hand quadrant of Table 2, those with an appreciable propensity for the nonpolar phase that did not become enriched in vertebrate fat, clearly show that bioaccumulation in some instances is *not* accurately predicted from partition coefficients.

Thus, K_{ow} alone is not sufficient for predicting bioaccumulation under environmental conditions where an even greater array of factors such as sorption to soils, volatilization, biological and nonbiological degradation can affect the ultimate chemical residues reached in animal tissues. In an analysis of quantitative structure-activity relationships of chemicals for use as a prebiological screen for ecotoxicologic effects, Gillett (1983) used partition coefficient, Henry's Law constant, and biodegradation half-life as a means of rapidly identifying chemicals with the potential for becoming environmental problems. When coupling a measure of environmental degradation with that of partition coefficient, Gillett observed that if the half-life in soil is < 4 days and the K_oINw < 300, then bioaccumulation is highly unlikely; but if the soil half-life is > 14 days and $K_{ow} > 3000$, then there is a considerable probability of accumulation.

TROPHIC PATHWAYS IN TERRESTRIAL SYSTEMS

Hazardous chemicals can be transferred from soils to terrestrial biota through several trophic pathways (Figure 1). The number of transfer steps in a pathway, such as soil to plant, plant to herbivore, livestock to human, is important because at each step opportunities are provided for excluding chemicals and for additional metabolic detoxications to occur. Nonetheless, some xenobiotics can reach biological concentrations in excess of those found in the surrounding soil after transfer through multicomponent foodwebs.

Under conditions of chronic exposure, ingestion is usually the most important route by which terrestrial animals are exposed to soil contaminants. Plants that have been contaminated due to root uptake of xenobiotics followed by translocation to the foliage are a likely vehicle for oral intake as are plants externally contaminated by soil splashed onto aboveground plant parts. In addition, vegetation can be contaminated by chemicals that volatilize from the soil and redeposit onto foliage.

Soil to Animal

Direct consumption of contaminated soils may be the most important route of exposure for hervibores. In a study of farm animals in Michigan where soils were contaminated with polybrominated biphenyls (PBB), Fries (in press) found that the BCFs (animal fat: soil) differed among species in a comparison of sheep, swine, dairy cattle, and beef cattle. BCFs were highest in swine and were proba-

TABLE 2. A total of 122 observations of bioaccumulation (BCF) in animal fat are tabulated as a function of partition coefficients (K_{ow}) for 68 chemicals. A comparison of numbers of observations falling in each quadrant of the table illustrates the positive, although imperfect, relation between K_{ow} and BCF (Garten and Trabalka 1983).

	Log K_{ow} (±0.5)								
Log BCF (±0.5)	-1	0	1	2	3	4	5	6	7
-5	1				1	6	1		
-4	1		1	1	5				
-3		2	6		8	5	3		
-2		2	2	6	6	3	1	1	
-1				1		1	3	3	1
0						3	10	18	2
1							6	9	2
2									1

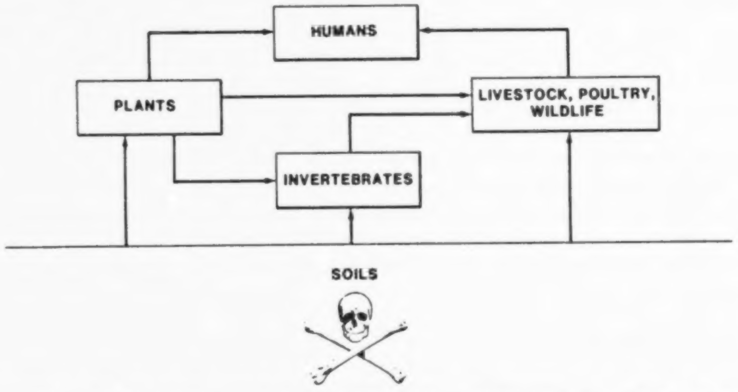

FIGURE 1. Major pathways by which hazardous chemicals in soils can reach terrestrial plants and animals.

bly the result of the greater soil ingestion that occurs during rooting by swine when compared with the feeding habits of other livestock (Fries and Marrow 1982). In addition, yearling heifers and beef calves had higher BCFs than cattle that had lactated, indicating that lactation provides a route for elimination of PBB residues from the body.

The importance of soil to animal exposures is further supported by studies of dioxin residues in animals at the Eglin Air Force Base Reservation in Florida and by laboratory studies documenting the bioavailability of soil-bound dioxins after ingestion by guinea pigs and rats (McConnell et al. 1984). From 1962–1970, an estimated 2.8 kg of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) was sprayed as a contaminant of the herbicide 2,3,5-trichlorophenoxyacetic acid to a 3.0 km^2 site used to test equipment for aerial spraying of defoliants (Young 1983). In field studies from 1973 to 1978, 21 of 63 animal species analyzed were positive for TCDD (Thalken and Young 1983). Body residues generally correlated with ambient soil concentrations and degree of animal contact with the soil. For example, beachmice, *Peromyscuc polionotus*, had measurable body residues of TCDD in the absence of a contaminated food source; however, these animals had considerable opportunity for ingesting contaminated soil during burrowing and grooming. The highest TCDD residues in liver and fetuses of beachmice occurred at the sites where soil concentrations of TCDD were highest. Males had a higher mean concentration of TCDD than did females, which the authors attributed to the females' ability to pass residues on to their pups and in so doing, to remove them from their own bodies. The females are so fecund, that an equilibrium state between dioxin in the body with that in the surrounding soil was never achieved.

The importance of soil contact to the transfer of contaminants from soil to animals is also reflected in numerous studies of soil and litter invertebrates at chemically contaminated sites. For example, TCDD in earthworms and soil were positively correlated at Seveso, Italy, where an accidental release occurred in 1976 from a chemical manufacturing plant (Martinucci et al. 1983). Dioxin residues in earthworms (three species of *Allolobophora* with gut contents removed before analyses) were 15 times greater than soil concentrations. Concentrations of TCDD in soil and earthworms were described by the equation $y = 2.38 + 0.96\ x$, $r = 0.97$ (Figure 2), where y is the $\log_{10}$ of TCDD $\mu g\ kg^{-1}$ in earthworms and x is the $\log_{10}$ of TCDD $\mu g\ kg^{-1}$ in soil. Based on their findings, the authors recommended the use of earthworms for monitoring contaminated sites because residues could be detected in earthworms when soil concentrations were below detection limits. An additional advantage to using earthworms and other soil invertebrates in bioavailability and bioaccumulation studies is that they reach equilibrium so much faster than larger animals.

Thus, direct contact with the soil can be important to the transfer of contaminants from soil to animals, and this route has been shown to be the most important contact for livestock in particular, and herbivores in general.

Soil to Vegetation

In plants, as with animals, uptake of organics is influenced by a number of factors. Molecular size is important; plant roots generally do not exclude small molecules. Polar compounds are taken up more readily than are nonpolar chemicals, but prediction of accumulation is confounded by the fact that polar substances are more susceptible to biochemical transformations and are less likely to be sequestered than are nonpolar molecules. Although lipophilic substances may not be readily translocated across plant cell walls to be internally incorporated in the plant, nonetheless, they can reach elevated concentrations through preferential adsorption from the soil onto the surface of roots and stems. In addition to the properties of xenobiotics that can influence uptake and accumulation, soil properties such as clay content, organic matter, and pH can influence uptake. Characteristics of specific plant species and strains can also influence bioaccumulation.

Although few studies have been conducted to examine bioaccumulation of chemicals in situations selected specifically to represent land treatment of organic wastes, numerous studies of agricultural chemicals, chlorinated hydrocarbons, and polycyclic aromatic hydrocarbons provide data pertinent to land treatment because the same types of chemicals may be present in land-treated wastes. Polycyclic aromatic hydrocarbons (PAHs) are of concern because they are present in many products, by-products, and wastes from the petroleum industry. In addition, PAHs as a group include a number of carcinogens and mutagens that are stable under environmental conditions and are lipid soluble, which favors accumulation in many organisms. An extensive review of the literature on PAHs in terrestrial ecosystems (Edwards 1983) revealed that almost all of the PAH research with terrestrial vegetation has been with benzo(a)pyrene (BaP) only. One of the few studies that has examined both vegetation and soil for concentrations of several PAHs was that of Wang and Meresz (1981). In this study, concentrations of 17 PAHs in the edible portions of onions, tomatoes, and beets were examined. BCFs for all the PAHs were less than 1 with greatest concentrations in onions (primarily in the peels) and lowest concentrations in tomatoes (also primarily in the peels). Similarly, Ellwardt (1977) found BCFs < 1 for 7 PAHs in potatoes grown in soil treated with contaminated compost.

In the above studies, concentrations of individual PAHs in vegetation ranged from 0.1 μg/g to levels too low for detection. In both studies, the summed concentration of all identified PAHs in the soil was less than 1 μg/g with each PAH contributing < 0.1 μg/g. Much greater concentrations may be expected in soil treated with organic wastes. PAH concentrations up to 300 μg/g near known PAH sources have been reported (Edwards 1983). In such highly contaminated soils, PAH concentrations in vegetation could reach relatively high levels even without bioconcentration. For example, analysis of vegetation from soil covering a coal tar waste disposal pit revealed individual PAH concentrations up to 2 μg/g with totals for 14 PAHs reaching 6 μg/g. Concentrations of the same 14 PAHs

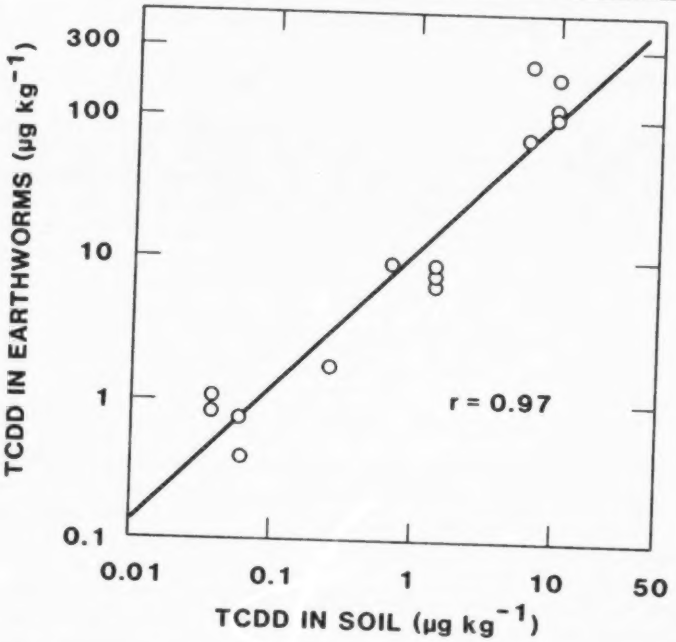

FIGURE 2. Concentrations of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) in earthworms were approximately fifteen times greater than TCDD soil concentrations found in the surrounding soil over a 150 m by 150 m area in Seveso, Italy. Concentrations of TCDD in soil and earthworms are described by the equation $y = 2.38 + 0.96 X$, where y is the $\log_{10}$ of TCDD in earthworms and X is the $\log_{10}$ of TCDD in soil (Martinucci et al. 1983).

(summed) in vegetation from a moderately contaminated area (i.e., near a coal-fired steam plant) did not exceed 0.1 μg/g.

While uptake by vegetation growing on land treated with organic waste may represent a potential transfer pathway for some xenobiotics, the advantages of having a vegetative cover on such sites should be considered. Besides the obvious positive aspects (e.g., erosion prevention, transpirational water losses resulting in decreased leaching to groundwater), plants may be important in the chemical transformation of hazardous chemicals to nonhazardous products. For example, Dorr (1970) found a decline in BaP in rye plants (*Secale cereale* L.) after their removal from a BaP source and attributed the decline to plant metabolism. Durmishidze et al. (1974) and Durmishidze (1977) demonstrated chemical transformations of BaP and benz(a)anthracene (mostly to organic acids) within a number of plant species. Edwards (1986) found that bean plants (*Phaseolus vulgaris* L.), chronically exposed for 30 days to ^{14}C PAHs, metabolized from 63% to 85% of the PAH assimilated. Intuitively, these kinds of data suggest that planting vegetation on land treatment sites should be encouraged. However, careful consideration should be given to that percentage of the xenobiotic that is not metabolized during chronic exposure and to the identity of hazardous metabolics potentially formed. In the case of PAHs, concentrations in vegetation will reflect concentrations in soil even with metabolism of the compound and without bioconcentration as discussed above.

In studies by Chan et al. (1978) PBB uptake by vegetable roots varied with species. BCFs (roots:soil) for carrots were higher than those for radishes and onions, and of these three vegetables only carrots showed PBB enrichment (BCFs greater than 1). Even when xenobiotics are not appreciably taken up by plant roots, the soil can still serve as a source of contamination due to vapor sorption by the plant above ground as demonstrated with DDT and soybeans by Beal and Nash (1971).

The influence of plant variety on contaminant absorption from soils is illustrated in studies of aldrin, dieldrin, and endrin uptake into several types of carrots (Lichtenstein et al. 1965; Hermanson et al. 1970). Concentrations of specific insecticides differed by as much as four-fold as a function of carrot variety although in all instances BCFs were less than unity.

Vegetation to Animals and Higher Trophic Level Interactions

Herbivores and some omnivores ingest large quantities of vegetation so that their energy and nutritional requirements can be met by a food high in fiber and low in energy, protein, and many essential trace elements. Thus, even low concentrations of organic xenobiotics in vegetation can theoretically lead to biologically significant exposures in herbivores. Yet it is generally predatory animals, those feeding at higher trophic levels, where enrichment in tissue concentrations of persistent, lipophilic xenobiotics has been shown to occur in terrestrial ecosystems.

The lack of evidence for a marked enrichment of xenobiotics through the vegetation to animal pathway could be due to differences in physicochemical properties of those substances likely to accumulate in plant tissue versus those likely to be sequestered in animal tissues. Alternatively, the fact that many common herbivores are large animals may be a more important consideration than the absolute quantity of food eaten. Kenaga (1972) pointed out that while larger animals eat more food than smaller, lighter animals, the latter group may be at higher risk of ingesting toxic doses of contaminants because of differences in the quantity of food consumed relative to body weights. While beef cattle consume approximately 1.5% of their body weight in food daily, a white mouse eats 12% and a hamster takes in 15%. Therefore, the quantity of contaminants ingested on a body weight basis would be greater for the smaller animals than for a larger animal feeding on a diet containing the same concentration of toxicant.

Further complicating comparisons of bioaccumulation at different trophic levels is the fact that BCFs for herbivores are usually reported on the basis of whole body residues relative to soil concentrations, whereas BCFs of predators are often calculated on the basis of residues in fatty tissues only (Moriarty 1983), which tends to yield higher BCFs for predators. Thus, valid comparisons of xenobiotic accumulation in animals at different trophic levels requires consideration of food consumption (and xenobiotic uptake) relative to body weights as well as residue analyses of comparable body tissues.

Nonetheless, some xenobiotics appear to be concentrated through food chains of terrestrial animals. For example, in a study of aldrin and dieldrin residues among vertebrates and invertebrates from two aldrin-treated cornfields in Missouri (Korschgen 1970), the lowest BCFs (0.74–3.5) were found in animals with a significant amount of plant matter in the diet. The highest BCFs (11–40) were found in toads, predaceous beetles, and garter snakes, which feed primarily on insects and earthworms. This pattern of greater xenobiotic accumulation at higher trophic levels was also observed by Brown and Brown (1970) in a subarctic environment where herbivorous vertebrates (red squirrel, willow ptarmigan) had the lowest residues of 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT) (1.97 and 3.40 ppm DDTR, respectively). Sparrows feeding on seeds and insects had intermediate concentrations of DDT and metabolites (11.1–17.4 ppm) whereas six species of birds with diets of insects and fish had the highest DDT residues (range 41.9-63.5 ppm).

IMPLICATIONS FOR LAND TREATMENT

Chemicals that accumulate in plants and animals have the potential for producing adverse toxicological effects under conditions of chronic exposure; hence, wastes that are candidates for land treatment must be evaluated for the presence of such compounds. Substances especially likely to bioaccumulate include nonpolar organics that are stable under environmental conditions. Many of these chemicals, such as halogenated hydrocarbons, could become problematic during land treatment even though they may be present in wastes in only trace amounts. The polycyclic aromatic hydrocarbons are among the classes of chemicals for which more studies are needed regarding their propensity to bioaccumulate.

Use of the natural, assimilative properties of soils to effect degradation and detoxication of waste chemicals holds promise as an effective and economical means of disposal; but in order to ensure safe disposal of chemicals on land, gaps in our knowledge of contaminant mobility and degradation must be filled. Of special importance is the need to extrapolate from indices of bioaccumulation that can be measured in the laboratory, to the actual behavior of chemical contaminants during various land treatment scenarios. In addition, research is needed to identify the ways in which waste disposal sites can be managed to enhance biological degradation and thereby reduce the potential for bioaccumulation. These studies will not only help to ensure the safety of land treatment practices, but will also help to fully realize the benefits of land treatment for waste disposal.

ENDNOTES

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[2] Publication No. 2653, Environmental Sciences Division, ORNL.

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SITE SELECTION FUNDAMENTALS FOR LAND TREATMENT

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ABSTRACT

Suitable degradable-waste land treatment (DWLT) requires the ready identification and quantitative measurement of site characteristics that control the stabilization and confinement of the polluting constituents. Land treatment systems involving degradable wastes are hiqhly site specific making the selection of the site criteria subject to personal judgment, depending primarily on different climatic patterns. Despite these difficulties, acceptable criteria and their latitudes were developed in this study.

The process for the screening and evaluating of fundamental criteria for site selection of suitable land treatment facilities is presented in five major steps.

STEP 1 was developed as a screening process requiring the accumulation of reconnaissance data for land locations suitable for the kind(s) of waste to be land treated. Step 1 was designed to eliminate the obvious unacceptable locations early in the selection process by (1) identifying the limiting features of the landscape, soil, hydrology, geohydrology of the sites for use as an DWLT facility and (2) identifying the level of constraints necessary to protect the health of mankind and the environment from undesirable deterioration.

STEP 2 was developed as a numerical rating process of acceptable landscape and topographic characteristics.

STEP 3 was developed as a numerical rating process of acceptable soil characteristics that influence pollutant control.

STEP 4 was developed to numerically rate acceptable hydrological and hydrogeographical characteristics of the site that influence pollutant retention.

STEP 5 was developed to provide the final numerical evaluation and comparative rating of the DWLT sites that were not eliminated in Steps 1 through 4.

Tables describing the site selection criteria were provided for numerical scoring of each characteristic included in Steps 2, 3, and 4. With Step 5, Table 5 was designed as a check sheet for summation and final site rating.

INTRODUCTION

Incomplete knowledge of ways to dispose of organic wastes, to insure their confinement, and to maximize biodegradation has led to a search for better site selection *criteria* for degradable-waste land treatment. Land treatment involves the application of waste on the soil surface or incorporation of waste into the upper layers of the soil to *degrade*, *transform*, or *immobilize* hazardous constituents present in the waste. It is considered as a viable waste management option. The soil is a key waste treatment system of the environment, since almost all wastes ultimately end up on the land. The air and streams are merely transport systems to return waste back to the land. Moreover, people are sensitive to dumping in the ocean, even to the point of supporting legislation prohibiting such aetion.

Site selections can be made which are suitable for DWLT facilities if all of the critical characteristics of the selections have been carefully evaluated and acceptable latitudes of the site characteristics have been set in terms of quantitative guidelines.

The principal objectives of this effort were to: (1) Provide methodology, in document form, for selecting suitable sites for land treatment of selected wastes based on a numerical rating scheme of factors influencing pollutant retention and stability; and (2) Identify those site criteria which can be managed and operated for acceptable performance as a system to utilize the natural biological, chemical, and physical processes in the soil for the purpose of degrading, attenuating, or otherwise rendering innocuous those wastes receiving such treatment.

The subordinate objectives provided for a step-by-step methodology to select specific sites to accommodate specific types of waste while diminishing any effects on human health and the environment. The land treatment site selection criteria process included five major screening steps which are:

STEP 1. Reconnaissance for prospective land areas, initial site quality screening, and elimination of obviously unacceptable locations,

STEP 2. Rating of specific landscape and topographic criteria of acceptable sites,

STEP 3. Rating of specific soil criteria of acceptable sites,

STEP 4. Rating of certain hydrological and geohydrological criteria of acceptable sites, and

STEP 5. Final site evaluation through accumulation of numerical values of STEPS 2, 3, and 4 with an orientation of single comparative rating values.

APPROACH

The conditions for the establishment of a degradable waste land treatment (DWLT) facility were described, based on an informed and identifiable selection process for a site, rather than by chance. Methodology was described for numerically rating various locations as to suitability for land treatment of selected wastes. A suitable site must provide conditions necessary to degrade organics, retain persistent organics, immobilize inorganics, and protect groundwater quality and other components of the environment.

This document identified acceptable and unacceptable land site characteristics and provided a capacity to delineate marginal characteristics which can be managed for acceptable performances. The procedure for site selection observed all restraints to assure that pollutants do not enter chain foods or even approach avenues leading to the chain food crops and to assure that the groundwater and surface water is maintained at the highest quality, free from chance pollution. This was accomplished through a land treatment rating system which was organized for convenience into five steps.

The final evaluations of the DWLT sites were compared on a basis of information entered in STEPS 2 through 4. The purpose of STEP 1 was for reconnaissance of the proposed site area(s) with a final screening to eliminate obviously unsuited sites. STEPS 2, 3, and 4 consider screening only of those sites retained after STEP 1. It is still possible to find some sites that are not acceptable after the first screening due to a combination of poorly suitable features or land features overlooked during the reconnaissance.

Appendix A provides supporting data for evaluation of the criteria of each STEP used for assessing the suitability of sites for an LT facility. Rating information and techniques were presented which are helpful for scoring selected criteria in the original U.S. EPA report (Fuller 1984). Appendix B provides examples for testing site selection criteria using actual field sites. These Appendices are omitted here but are in the original report.

PROCEDURE

Step 1—Reconnaissance for Acceptable Land Areas and Initial Screening

This initial screening was designed to identify and locate topographic and water features in the target area for the purpose of: (1) saving time and effort by eliminating areas that do not meet the minimum requirements for land treatment; and (2) identifying potential problems reflected in the physical, cultural, or social aspects of the area. It was presumed that the areas eliminated, at this point, clearly do not have the characteristics necessary to ensure adequate protection of groundwater or surface water or to provide adequate waste treatment and stabilization.

Table 1 lists unacceptable location features which will result in the elimination of certain undesirable areas from further consideration as sites for land treatment. The last column in Table 1 identifies the specific land feature that eliminates the site or requires unusual corrective treatment to be acceptable. Because this step is an elimination/no elimination process, no numerical values need to be involved.

TABLE 1. Unacceptable location features which will result in the elimination of a site from further consideration for land treatment: STEP 1.

The proposed site is not situated such that the treatment area of the facility will be located--unless drastically altered to insure complete containment of hazardous constituents by construction management.	Severe Limitations E
A. On unsuitable landforms[1] of	
Floodplains: 100 year (U.S. EPA Fed. Reg. Sec. 264.18(16), p. 32290).	
Moraine: Highly heterogeneous materials of geologic debris including sands, gravels, stones, boulders, and rock fragments all mixed together.	
Drumlins: Limited areas on steep slopes.	
Filled Valleys: Highly heterogeneous material	
Coastal Plains: Highly heterogeneously mixed geologic debris that is usually very porous.	
Deltas: Frequently flooding.	
Tidal Flats: Frequent flooding, salty.	
Sand Dunes: Wind erosion, shifting sands, highly porous, poor attenuation.	
B. Over unsuitable geological and hydrogeological formation	
Karst: Porous, fractured, stratified limestone.	
Volcanic Cinders and cinder materials: Porous, coarse texture.	
Rock Outcrops.	
C. On unsuitable hydrological areas of	
Seasonally high water table: Within 2 meters of the surface; may be acceptable with adequate drainage.	
Wetlands: Permanently swampy and wet, bogs.	
Within 150 meters of a well that is or will be a source of water supply for any use.	
D. On unsuitable soils with	
pH values less than 5.5	
Shallow depth of soil, < 2 ft.	
Slopes greater than 6%.	
Highly restrictive subsoils completely impermeable within 2 feet meter depth.	
Excessively permeable sands, gravels, rocks, and stones.	
Classifications of saline, saline/alkaline, and alkaline land.	
Severe soil and/or wind erosion.	
E. On undesirable land use areas of	
Polluted and/or contaminated land.	
Upwind of population centers.	
Rough and broken land, stone, and cobbles predominate.	
Wilderness areas inaccessible to operations.	

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[1] Insert E (elimination) in checklist at the right, if applicable.

Site:________________

Step 2—Rating Landscape and Topography Characteristics

Landscape. Landscape refers to the way the land looks. Landscape features can determine the public attitude toward the facility. Changes in landscape from that of the original nearly always evoke local comment and often initiate adverse public reactions. Photographs and elevation maps identifying the major landscape features before establishment of the LT facility are a good practice and provide a basis for returning the land, as nearly as practical, to its original condition. Evaluating landscapes numerically may not always be possible since the evaluation process is highly subjective.

Topography. Topography describes the configuration of a surface, including its relief and the position of its natural and man-made features. Topography influences surface runoff, soil depth, evapotranspiration, rainwater infiltration, extent of soil erosion hazard, soil temperature, kind of vegetation, etc.

Three site characteristics are evaluated at STEP 2, Table 2: (1) land surface slope, (2) susceptibility to soil erosion, and (3) necessary site modification to allow land treatment to be undertaken with assurance of hazardous waste confinement. A numeral designation of 4 indicates a most desirable feature and 1 the least desirable feature. Each of the three characteristics is evaluated independently with the sum of the three representing the overall STEP 2 quantification.

No good purpose is served if the applied wastes are permitted to migrate horizontally across the soil surface and end up in a runoff control or treatment pond. Should this be permitted, the original objective of land treatment is defeated and one may as well have begun with a treatment pond. The advantages of a land treatment site favor flat or slightly sloping locations free from surface erosion. Established guidelines for slope tolerance and threshhold values must be cautiously flexible, with provision made for immediate adjustments as new information becomes available. The most effective guidelines, at this time, must originate from experience with soil erosion and runoff evaluations developed by the USDA Soil Conservation Service (SCS) and SCS personnel experienced in soil conservation.

Slope categories were established at values ranging from 0 to 6% with a provision for earthwork to erect berms, diversion ditches, contouring, terracing, grass strips, and other designs to insure confinement on the treatment area along with a warning to avoid erosion-prone soils and landscapes known to have erosion problems. The U.S. Environmental Protection Agency regulations require all runoff and runon be controlled. This also applies to adjacent land that could supply runon water. Deposits of erosion materials must be avoided by taking heavy rainstorm environments (climates) into consideration.

Step 3—Rating of Soil Characteristics

STEP 3 was established to quantitatively rate soil properties which predominately affect the performance of biodegradation, immobilization, and attenuation at any given site for the control of hazardous waste pollutants.

TABLE 2. The STEP 2 rating of landscape and topographic characteristics on a basis of numerical classes.

Landscape and Topography	Rating (p[illegible]					Score*
	4	3	2	1	E	
Predominant slope range - %	1-2	0-3	2-4	4-6	>6	
Soil erosion susceptibility class (USDA-SCS 1983)	no erosion problems USDA-SCS Class 1	slight erosion: easily corrected USDA-SCS Class 2	slight, but not easily corrected USDA-SCS Class 2	serious erodability, can be corrected USDA-SCS Class 3	serious erosion not correctable USDA-SCS Class 3 & 4	
Land capability classification-% (USDA-SCS 1973)	cultivated Class I-100	cultivated with modification Class I-75% Class II-25%	cultivated Class I-50% Class II-50%	cultivated Class I-25% Class II-75% Non-cultivated pasture Class II-75% Class III-25%	cultivated Class IV through Non-cultivated Class VIII	
Land site modification; filling; clearing of vegetation; diking; barriers; construction	none	small area, 10% low cost	acceptable area of 10-20% moderate cost involved	large area of 20-50% costly	large area costly >50%	
Average or Sum						

* The scores for each feature are recorded in the last column and summed on the last line. Any value of E eliminates the location as a possible site.

Site:____________________

Table 3 was designed to provide for the establishment of a numerical point rating system with a final summation score that designates the degree of suitability of soils for hazardous waste land treatment. There are eight soil parameters listed which can vary in quality from 1 to 4. The highest single parameter rating is 4 and lowest is 1. For those soils found wholly unsuitable at this stage, a category of E (elimination) is provided. Category E seldom is expected to be present at STEP 3, but was included to accommodate cases where the discovery of unusual or masked properties were overlooked during earlier Steps.

Measurement of all eight soil parameters—particle size distribution, hydraulic conductivity (intrinsic permeability), soil depth, pH, cation exchange capacity, drainage class, available water holding capacity, and restrictive subsoil layer—may not always be necessary to identify an acceptable site. It must be recognized that the score based on soil characteristics at STEP 3 will be higher than STEP 2 because of the greater number of characteristics listed for evaluation. The final summation, therefore, will be numerically weighted in favor of soils, which at this time appear to be the best. These items require actual field testing before final adoption. Appendix A of the original report provides specific data and evaluation of each of the soil characteristics scored in Table 3, STEP 3.

TABLE 3. The STEP 3 rating scale of soil characteristics for DWLT site selection.

	Rating (points)					
Soil Parameters	4	3	2	1	E	Score*
Salt and alkali (%)	0-0.15	0.15-0.35	0.35-0.50	0.50-0.65 reclaimable	>0.65	
Hydraulic conductivity; cm/sec (in top 60 cm of soil)	10^{-3} to 10^{-2}	10^{-3} to 5×10^{-4} or 10^{-2} to 5×10^{-2}	5×10^{-4} to 10^{-4} or 5×10^{-2} to 10^{-1}	10^{-4} to 5×10^{-5} or 20^{-1} to 5×10^{-1}	$<0.5\times10^{-5}$ or $>5\times20^{-1}$	
Available water holding capacity (in H_2O/ft of soil depth)	>1.5	<1.5 to 1.0	<1.0 to 0.75	<0.75 to 0.5	<0.5	
Wetness class	well drained	moderately well drained	somewhat poorly drained, somewhat excessively drained	poorly drained	very poorly drained, or excessively drained	
Particle size distribution (top 60 cm of soil)	loam, silt loam, sandy clay loam	sandy loam, silty clay loam, clay loam	sandy clay, silty clay	loamy sand, silt	sand, clay, muck	
pH	>7.0	<7.0 to 6.5	<6.5 to 6.0	<6.0 to 5.5	<5.5	
Cation exchange capacity (mg/100 g)	>25	<25 to 15	<15 to 10	<10 to 5	<5	
Soil depth (m)	>5	<5 to 3	<3 to 2	<2 to 1	<1	
Restrictive subsoil layer	None	slightly restrictive	moderately restrictive	highly restrictive	severely restrictive	
Sum						

*The scores for each soil parameter are recorded in the last column and summed on the last line. Any value of E eliminates the locations as a possible site, and evaluation stops here.

Site:______________________________

Step 4—Rating Hydrological and Hydrogeological Characteristics

STEP 4 was developed to evaluate important hydrological and hydrogeological site characteristics such as: (1) Depth to bedrock, hardpan, or other impervious layers and other significant impeding geologic formation; (2) Depth to groundwater including seasonal perched water and regional water levels; (3) Groundwater and surface water quality.

A rating chart (Table 4) takes into account the hydrogeological and hydrological characteristics that affect the selection of an acceptable land treatment site.

The four hydrological characteristics evaluated in STEP 4 (Table 4) are: depth to groundwater, depth to seasonal high water table, depth to bedrock, and groundwater quality. Numerical scoring, ranging from 1 to 4, is provided. Again the 1

TABLE 4. The STEP 4 rating of hydrological and hydrogeographical characteristics for DWLT site selection.

Hydrogeographical and Hydrological Parameters	Rating (points)					
	4	3	2	1	E	Score*
Depth to groundwater (m) (regional)	≥50	50 to 20	20 to 3	3 to 2	<1	____
Depth to seasonal high water table (m)	≥6	6 to 4	4 to 3	3 to 2	<1	____
Depth to bedrock (m)	>10	10 to 6	6 to 3	3 to 1	<1	____
Groundwater quality EC = mmhos/cm	0.75	0.75 to 1.5	1.5 to 3.0	3.0 to 7.5	>10	____
Sum						

*The scores of each parameter are recorded in the last column and summed on the last line. Any value of E eliminates the location as a possible site.

Site:____________________

value is least suitable and 4 the most suitable with E the designate for site elimination. Permanent and seasonal groundwater depths of less than 1 m are sufficient to eliminate the site for DWLT. Groundwater depths of 20 m or greater represent hydrological characteristics that are highly desirable for LT because of the favorable treatment depth and safety buffer.

The hydrogeology also is important to site design and development in a manner to protect and minimize the impact on groundwater quality. Unacceptable hydrogeologic conditions should dictate the elimination of the site for DWLT or necessitate alterations to render it acceptable. Acceptability of a site at STEP 4 assumes precipitation, evapotranspiration, and other climatological conditions have been taken into consideration in site selection as an essential factor in water quality recharge.

Shallow soils (<2 m), particularly over loose gravel, stones, boulders, cracks, karst, etc., and sands (>2 mm) that permit rapid flow must be avoided since these characteristics have a high potential for rapid transmission. On the other hand, unlike sites for LT of "nonhazardous" waste waters, surface soils for DWLT should not be so rapidly permeable nor subsoils so slowly permeable (less than 0.5 cm hr^{-1}) that installation of subsurface drainage systems becomes necessary. Locations where slowly permeable subsoil layers (<0.5 cm hr^{-1}) are indigenous within a meter of the surface, should be excluded as a suitable site, particularly in climates where rainfall is known to substantially contribute to groundwater recharge or where irrigation or waste water applications are expected to migrate rapidly to groundwater levels.

Depth to groundwater of less than 1.5 m for a land treatment site is unsuitable for slow or rapid waste water applications. The U.S. Environmental Protection Agency regulations (1982) require 1.0 m separation between treatment zone and any water table. A separation depth of 3 m or greater is most desirable, partly because of the unfavorable problems associated with the development of a polluting water mound and a need to insure completion of aerobic waste treatment, and partly because of the chance creation of a need for costly drainage facilities in cases within shallow depths to groundwater. Depth to groundwater can become the limiting rating value of soil depth, (rather than depth to bedrock) since the water level defines the effective drainage depth.

Some lands are subjected to seasonal high water tables that frequently fluctuate due to subsurface restriction layers, claybed lenses, etc., that temporarily perch water. Seasonal high water table is a zone of saturation at the highest average depth during the wettest season. It is at least 15 cm thick, persists in the soil for more than a few weeks, and is within 2 m of the soil surface.

Step 5—Final Site Evaluation

An evaluation of prominent individual and STEP 2, 3, and 4 characteristics is presented in Table 5 as STEP 5 for final screening and selection of the most suitable DWLT sites. Since none of the individual characteristics exceed the U.S. Environmental Protection Agency (1982) regulations, a summation of individual and/or STEP 2, 3, or 4 scores produces a valid numerical evaluation for each site. All unsuitable sites should have been eliminated before STEP 5 is reached,

TABLE 5. The STEP 5 rating of land characteristics for final screening for the selection of suitable LT sites.

Characteristic Used in Evaluating LT Sites	Individual Score	Step	
		Number	Scores
Reconnaissance for elimination of unsuitable sites	________	_____	_____
Prominent slope range	________		
Soil erosion	________		
Land capability class	________		
Land site modification	________	_____	_____
Soil salinity	________		
Hydraulic conductivity	________		
Available water holding capacity	________		
Drainage class	________		
Particle size distribution	________		
pH (Acidity)	________		
CEC (Cation exchange capacity)	________		
Soil depth	________		
Restrictive subsoil layer	________	_____	_____
Depth to groundwater	________		
Depth to seasonal high water table	________		
Depth to bedrock	________		
Groundwater quality	________	_____	_____
Sum			

LT Site Identification:______________________________

Relative Rank:____________________ Date Evaluated:__________

Evaluator(s):______________________________

therefore, all sites that reach STEP 5 are acceptable although all may not be equally suitable. Each proposed site must complete each STEP and have the results entered into appropriate spaces in Table 5 or STEP 5. A summation of the individual characteristic scores (evaluations) constitutes the final ranking. This figure is entered on the sheet beneath the space reserved for the HWLT site identification. When all of the sites are numerically scored, they are oriented according to "relative rank" (e.g., 1, 2, 3, 4, etc.). Those sites receiving the highest numerical scores are considered the most suitable. The STEP 5 final screening sheet is then signed by the evaluator(s) and dated. The STEP 5 rating sheet becomes a work sheet for site development and design modifications as dictated by the nature of the degradable waste to be land treated.

CONCLUSIONS

(1) This study identified readily measurable site selection criteria for choosing the most suitable locations for degradable-waste land treatment facilities.

(2) A five-step process for screening and evaluating the most suitable land area for an HWLT site was developed and tested for validity.

(3) Five tables were prepared for numerical marking of the five-step critical evaluation criteria.

(4) Each STEP delineates specific fundamental criteria of interest.

STEP 1 was developed as a reconnaissance and screening process to roughly evaluate proposed sites and eliminate the obviously unsuitable.

STEP 2 was developed as a numerical rating process for evaluation of landscape and topographical characteristics.

STEP 3 was developed as a numerical rating process for evaluating soil characteristics.

STEP 4 was developed as a numerical rating process for evaluating hydrological and hydrogeological characteristics.

STEP 5 was developed to finally accumulate numerical values of steps 2, 3, and 4 into a final site evaluation and a final comparative rating.

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OCCURRENCE AND FATE OF CONSTITUENTS IN MUNICIPAL SLUDGE APPLIED TO LAND

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INTRODUCTION

Many municipal sewage treatment agencies have elected to utilize the plant nutrients present in municipal sewage sludge through a land application program. Sludge is applied to the land during the growing season in quantities sufficient to satisfy plant requirements. The organic material in municipal sludge also can be used to increase the humus content of the soil by application in excess of plant requirements. Such organic matter buildup can be useful especially for strip-mine land with little or no top soil.

Since municipal raw sewage contains virtually all of the wastes from man's activities, the sludge resulting from the treatment of this sewage will contain these same products. The presence and quantities of specific compounds in a municipal sludge will depend upon the nature of the activities served by a particular municipal wastewater treatment facility. There is concern on the part of regulatory agencies that the use of municipal sludge for fertilizing plants and building top soil can result in the transfer of certain constituents present in the sludge into plants, soil, and water. Obviously, such transfer could eventually affect man, who is an intricate part of the food chain.

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The Metropolitan Sanitary District of Greater Chicago (District) like many other municipalities utilizes some of its sludge in land application programs. The largest District sludge application to land program is located in Fulton County, Illinois. At this site, the District owns over 15,000 acres of land to which sludge is applied at the rate of about 25 dry tons/acre/year to former strip mined soils planted mainly with corn. Much of the data presented in this paper was extracted from the extensive monitoring which the District has done at the Fulton County site. The sludge applied at this site is anaerobically digested sludge that was transported to storage lagoons at the site before application.

District sludge and all municipal sludge is not exempted under the Resource Conservation and Recovery Act (RCRA). All municipal sludge must be subjected to the so-called EP (Extraction Procedure) toxicity test to determine if they are hazardous. In rule 261.24 (Hazardous Waste Management System, Federal Register, May 19, 1980), the United States Environmental Protection Agency (USEPA) classified a sludge as hazardous if its extract contains any of the contaminants at a concentration equal to or greater than the respective value shown in Table 1. Municipal sludge could be classified as hazardous if it failed to pass the EP toxicity test.

The District has performed the EP toxicity test on its various sludges to determine whether the resulting extracts exceeded the levels shown in Table 1. The range of metals found in District sludges is shown in Table 2, and that of pesticides is presented in Table 3. No extract exceeded the concentrations shown in Table 1. Therefore, no District sludge would be classified as hazardous. Obviously, if the sludges from a large metropolitan area such as greater Chicago are nonhazardous, there is a clear implication that most municipal sludges would be classified as nonhazardous.

TABLE 1. Limits of contaminants in extracts from sludges according to USEPA Rule 261.24.

Contaminant	Maximum Concentration (mg/l)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
2,4-D	10.0
Silvex	1.0

TABLE 2. Ranges of metal concentrations in extracts from metropolitan sanitary district of greater Chicago sludges.[a]

Sludge Source (No. of samples)	Ranges of Metal Concentration (mg/l)							
	As	Ba	Cd	Cr	Pb	Hg[b]	Se	Ag
Heat-Dried Sludge (21)	<0.2	<0.2	0.14-0.59	0.09-0.65	<0.02-0.23	<0.2-2.4	<0.2	<0.02
Nu Earth (6)	<0.2	<0.2	<0.02-0.22	0.19-0.42	0.06-0.23	<0.2-1.2	<0.2	<0.02
West-Southwest Digester Drawoff (30)	<0.2	<0.2	<0.02-0.08	0.06-0.23	<0.02-0.12	<0.2-5.8	<0.2	<0.02
Calumet Digester Drawoff (30)	<0.2	<0.2	<0.02	<0.02-0.39	<0.02-0.14	<0.2-3.7	<0.2	<0.02
Hanover Park Digester Drawoff (20)	<0.2	<0.2	<0.02-0.05	0.03-0.60	<0.02-0.17	<0.2-2.7	<0.2	<0.02
John E. Egan Digester Drawoff (30)	<0.2	<0.2	<0.02-0.10	0.02-0.11	<0.02-0.13	<0.2-2.5	<0.2	<0.02
West-Southwest Lagoon Sludge (13)	<0.2	<0.2	<0.02-0.03	0.11-0.27	<0.02-0.12	<0.2-7.8	<0.2	<0.02
Hanover Park Lagoon Sludge (2)	<0.2	<0.2	<0.02	0.06	<0.02	1.0-2.6	<0.2	<0.02
North Side Sludge (30)	<0.2	<0.2	<0.02-0.05	<0.04-0.25	<0.04-0.16	<0.2-3.8	<0.2	<0.02
Lemont Sludge (7)	<0.2	<0.2	<0.02	<0.04	<0.04-0.07	0.2-3.7	<0.2	<0.02

[a] Extractions performed according to the procedure on pp. 33127-33128 of the *Federal Register* May 19, 1980.

[b] Results in milligrams per liter, except for Hg, which is given in micrograms per liter.

TABLE 3. Ranges of pesticide concentrations in extracts from metropolitan sanitary district of greater Chicago sludges.[a]

Sludge Source	Number of Samples	Toxa-phene	Endrin[b]	Lindane	Methoxy-chlor	2,4-D	Silvex
		Ranges of Pesticide Concentration (mg/L)					
Heat-Dried Sludge	2	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
Nu Earth	2	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
West-Southwest Digester Drawoff	2	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
Calomet Digester Drawoff	2	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
Hanover Park Digester Drawoff	1	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
John E. Egan Digester Drawoff	1	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
North Side Sludge	1	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1
Lemont Sludge	1	<0.2	<1.0	<0.1	<0.1	<0.1	<0.1

[a] Extraction performed according to procedure on pp 33127-33128 of the *Federal Register* May 19, 1980.

[b] Results in milligrams per liter, except for Endrin, which is given in micrograms per liter.

This paper discusses the presence of metals and organic compounds in municipal sewage systems and municipal sludge. Information also is provided on the fate of these constituents in the soil, plants, and animals at sites to which municipal sludge was applied.

OCCURRENCE OF TOXIC POLLUTANTS IN RAW SEWAGE AND TREATED EFFLUENT

Occurence of Heavy Metals

Twenty-four hour composite samples of the influents to the various District treatment facilities are analyzed for heavy metals at least once every eight days. The average concentrations of heavy metals observed in municipal raw sewage during 1983 at the District treatment facilities are presented in Table 4. For a number of the metals, such as cadmium and nickel, the influent concentrations are often below detection. Thus, the average concentrations for the various treatment facilities are within a narrow range; e.g., cadmium ranged from 0.02 mg/L to 0.03 mg/L. Iron and copper are the two predominant metals in the sewage. Average iron concentrations ranged between 0.9 and 3.5 mg/L and average copper levels were from 0.06 to 0.30 mg/L during 1983.

The effluent from the District treatment facilities is sampled daily using automatic composite samplers. The average effluent heavy metals concentrations for the various facilities are presented in Table 5. Substantial removals are observed for those metals which occur in the influents. The effluent concentrations for a number of the heavy metals are generally below detection. The average effluent cadmium concentrations ranged from 0.0 to 0.002 mg/L. Copper effluent concentrations averaged between 0.004 and 0.023 mg/L for the various treatment facilities.

Occurrence of Organic Priority Pollutants

The District, like many municipalities, samples the raw sewage and final effluents of each of its treatment facilities to determine the concentrations of the organic priority pollutants that are present. A summary of the results for influent samples collected over the period of June through September 1984 is presented in Table 6. This table shows the range of concentrations of the organic pollutants detected in at least one sample. The data have been grouped together for the three major treatment facilities and four smaller facilities. The organic pollutants are grouped into four analytical divisions: volatile, acid extractable, base/neutral extractable, and pesticides.

Out of 106 organic priority pollutants analyzed, only 37 pollutants were found in at least one influent sample. The compounds most frequently detected in the influent sewage were ethyl benzene, chloroform, 1,1,1-trichloroethane, dichloromethane, phenol, and several of the phthalate compounds. The concentrations of the detectable compounds observed in the raw sewages were less than 50 μg/L.

TABLE 4. Average influent concentrations of heavy metals observed at district facilities during 1983.

	Average Concentration*					
Pollutant	Calumet	North Side	West-Southwest	John E. Egan	Hanover Park	O'Hare
Cadmium	0.02	0.02	0.02	0.03	0.03	0.02
Chromium	0.09	0.09	0.31	0.14	0.05	0.15
Copper	0.06	0.11	0.21	0.30	0.21	0.23
Iron	3.5	1.1	3.6	2.4	0.9	1.6
Lead	0.11	0.04	0.09	0.05	0.04	0.06
Mercury	0.2	0.2	0.3	0.5	0.4	0.5
Nickel	0.1	0.1	0.2	0.1	0.1	0.1
Zinc	0.4	0.2	0.4	0.5	0.2	0.6

*Concentration in mg/l except for mercury which is expressed in µg/l. Any sample value below detection was set at detection limit for purposes of averaging.

TABLE 5. Average effluent concentrations observed at district facilities during 1983.

Pollutant	Average Concentration*					
	Calumet	North Side	West-Southwest	John E. Egan	Hanover Park	O'Hare
Cadmium	0.00	0.00	0.002	0.00	0.002	0.00
Chromium(T)	0.003	0.001	0.021	0.00	0.008	0.00
Copper	0.005	0.005	0.023	0.004	0.017	0.004
Iron	0.49	0.002	0.23	0.0	0.00	0.0
Lead	0.00	0.01	0.019	0.11	0.009	0.012
Mercury	0.03	0.0	0.20	0.0	0.0	0.0
Nickel	0.0	0.0	0.125	0.0	0.0	0.0
Zinc	0.12	0.02	0.083	0.02	0.00	0.075

*Concentration in mg/l except for mercury which is expressed in μg/l.
(T) = Total

TABLE 6. Range of priority organic pollutants found in influents at district treatment facilities (over period of June through September 1984).

Pollutant	Concentration Range µg/l Major Facilities	Smaller Facilities
Volatiles (Purgeables)		
Dichloromethane	0.7 to 11.1	nd to 26.5
1,1-Dichloroethane	nd to 1.1	nd to 1.5
Trans-1,2-Dichloroethene	nd to 4.6	nd to 27.9
Chloroform	2.9 to 7.3	1.3 to 8.8
1,2-Dichloroethane	nd to 2.5	nd
1,1,1-Trichloroethane	4.1 to 53.8	1.5 to 4.2
Trichloroethene	1.2 to 44.1	nd to 7.4
Benzene	nd to 45.3	nd
Tetrachloroethene	2.6 to 29.6	nd to 8.1
1,1,2,2-Tetrachloroethane	nd to 10.9	nd to 7.3
Toluene	nd to 42.4	1.1 to 24.6
Ethylbenzene	nd to 20.5	nd to 69.9
Acid Extractables		
Phenol	0.8 to 22.4	nd to 27.4
2-Nitrophenol	nd	nd to 1.8
2,4-Dimethylphenol	nd to 2.5	nd to 3.7
2,4,6-Trichlorophenol	nd	nd to 0.6
Pentachlorophenol	nd	nd to 1.9
Base/Neutral Extractables		
1,4-Dichlorobenzene	nd to 2.9	nd to 2.0
1,2-Dichlorobenzene	nd to 1.8	nd to 2.0
Isophorone	nd to 1.3	nd to 0.5
Naphthalene	1.4 to 2.8	nd to 4.1
Dimethylphathalate	nd to 0.8	nd to 1.2
2,6-Dinitrotoluene	nd to 0.5	nd
Fluorene	nd to 0.5	nd to 0.9
Diethylphthalate	0.8 to 5.1	nd to 15.3

nd = NOT DETECTED

Major facilities include Calumet, West-Southwest and North Side (Sewage Treatment Works).

Smaller facilites include John E. Egan, Hanover Park, O'Hare and Lemont (Water Reclamation Plants).

TABLE 6. Continued.

Pollutant	Concentration Range µg/l Major Facilities	 Smaller Facilities
N-Nitrosodiphenylamine	nd	nd to 0.7
Phenanthrene	0.9 to 1.9	nd to 2.1
Anthracene	nd	nd to 0.7
D-n-butylphthalate	1.9 to 9.5	1.0 to 26.6
Fluoranthene	nd to 1.9	nd to 1.0
Pyrene	nd to 0.6	nd to 0.7
Butyl benzyl phthalate	1.1 to 2.5	0.6 to 10.0
Bis(2-ethylhexyl)phthalate	6.2 to 18.9	2.2 to 107
Di-n-octylphthalate	nd to 1.5	nd to 5.0
Pesticides		
Lindane	0.02 to 0.2	nd to 0.06
Heptachlor Epoxide	nd to 0.15	nd
Dieldrin	nd to 0.02	nd

nd = NOT DETECTED

Major facilities include Calumet, West-Southwest and North Side (Sewage Treatment Works).

Smaller facilites include John E. Egan, Hanover Park, O'Hare and Lemont (Water Reclamation Plants).

The concentrations of organic pollutants found in the effluents from the major and smaller District treatment facilities during the period of June through September 1984 are summarized in Table 7. The data indicate that the number of pollutants detected and their respective concentrations were reduced from that observed in the influents. Only 17 organic compounds were found in at least one sample. The pollutants occurring most frequently were chloroform, dichloromethane, and some of the phthalate derivatives. The effluent concentrations were less than 22 µg/L and generally less than 10 µg/L.

The influents and effluents at each of the District treatment facilities are also sampled and analyzed quarterly for PCBs. The average PCB concentrations observed in 1983 and 1984 are summarized in Table 8. The influent concentrations varied between 0.04 µg/L and 1.60 µg/L. The effluent concentrations were much lower, ranging between <0.02 µg/L and 0.17 µg/L over the two year period.

These data indicate that no organic priority pollutant is present at a concentration which would present any problem to the treatment facilities.

TABLE 7. Range of priority organic pollutants found in effluents at district treatment facilities (over period of June through September 1984).

Pollutant	Concentration Range µg/l Major Facilities	Smaller Facilities
Volatiles (Purgeables)		
Dichloromethane	0.5 to 3.4	nd to 11.5
Chloroform	1.5 to 6.3	nd to 8.6
1,1,1-Trichloroethane	nd to 13.4	nd to 4.4
1,2-Dichloropropane	nd	nd to 2.4
Trichloroethene	nd to 3.7	nd
Tetrachloroethene	nd to 5.1	nd to 3.1
1,1,2,2-Tetrachloroethane	nd	nd to 2.9
Acid Extractables		
Phenol	nd to 0.8	nd to 3.3
Base/Neutral Extractables		
1,4-Dichlorobenzene	nd to 0.8	nd
Diethylphthalate	nd	nd to 0.8
D-n-butylphthalate	nd	1.8 to 9.1
Fluoranthene	nd	nd
Butyl benzyl phthalate	nd to 2.0	0.6 to 1.6
Bis(2-ethylhexyl)phthalate	nd to 22.1	12.3 to 18.1
D-n-octylphthalate	nd to 1.6	nd to 10.5
Pesticides		
Lindane	nd to 0.02	nd to 0.01
Heptachlor Epoxide	nd to 0.005	nd

nd = NOT DETECTED

Major facilities include Calumet, West-Southwest and North Side (Sewage Treatment Works).

Smaller facilities include John E. Egan, Hanover Park, O'Hare and Lemont (Water Reclamation Plants).

TABLE 8. PCB concentrations in raw sewages and effluents at district treatment facilities during 1983 and 1984.

Sample Source	PCB Concentration in µg/l* 1983	1984
John E. Egan		
Raw	0.20	0.34
Effluent	<0.02	0.11
North Side		
Raw	0.45	0.13
Effluent	0.16	0.02
Havover Park		
Raw	0.07	0.05
Effluent	0.04	0.05
O'Hare		
Raw	0.05	0.13
Effluent	<0.02	<0.02
West-Southwest		
Raw, Southwest	1.60	0.96
Raw, West Side	0.55	0.67
Effluent	0.03	0.10
Calumet		
Raw	0.58	0.41
Effluent	0.07	0.17
Lemont		
Raw	0.04	0.14
Effluent	0.02	0.10

*Average of four samples each year.

OCCURRENCE OF POLLUTANTS IN SLUDGE

Occurrence of Heavy Metals

Most of the metals occurring in the raw sewage are retained in the sludges produced at municipal sewage treatment facilities. The treatment processes create conditions conducive to formation of insoluble forms, especially of the heavy metals. Principal forms include hydroxides, sulfides, oxides, and solid-organo compounds. The metal content of municipal sludge will reflect the quality of the entering raw sewage.

Sludges at all District facilities are routinely sampled and analyzed for metals. Table 9 presents sludge metal data compiled in 1984. Sludge produced in 1984 included digester drawoff from the West-Southwest, John E. Egan, Calumet, and Hanover Park facilities and primary plus waste-activated sludge from the North Side, Lemont, and O'Hare facilities. Lagoon sludge is produced at the West-Southwest facility and is distributed for nonfood chain purposes throughout the greater Chicago area. Metal concentrations are highly variable as would be expected in such a large area with diverse drainage basin characteristics. Cadmium levels, for example, ranged from 25 to 252 mg/kg.

Occurrence of Organic Pollutants

The organic priority pollutants which were detected in digested and waste activated sludges from various District treatment facilities are summarized in Tables 10 and 11. The samples were daily composites taken twice at each facility over the period of June through September 1984.

Out of the 106 organic priority pollutants analyzed, only 41 pollutants were detected in at least one sludge sample. The pollutants detected most frequently were toluene, trans-1,2-dichloroethane, chlorobenzene, and lindane.

Several organic pollutants which were not detected in the influent raw sewage samples were found in at least one District sludge sample. Some of these included chloromethane (nd to 29 ppb), chlorobenzene (nd to 20 ppb), nitrobenzene (nd to 42 ppb), and chrysene (nd to 63 ppb). On the other hand, several compounds, although detected in the influent raw sewage, were not detected in the sludges. These included 1,1,2,2-tetrachloroethane and dimethylphthalate.

The average PCB concentrations observed in various District treatment facility sludges are given in Table 12. These data represent averages of four samples taken each year. The average concentrations ranged from 0.001 mg/kg to 0.167 mg/kg on a wet weight basis.

FATE OF METALS IN MUNICIPAL SLUDGE APPLIED TO LAND

Soils and Plants

Research dealing with the application of sludge to land over the past twenty years has focused on the fate of the heavy metals contained in the applied sludge.

TABLE 9. Heavy metal concentrations of sludges from the Metropolitan Sanitary District of Greater Chicago wastewater treatment facilities and storage areas in 1984.

Source	Cd	Cr	Cu	Pb	Ni	Zn	Hg
	-----------------------	------------	mg/kg dry solids	------------	------------	-----------------------	µg/kg dry solids
Digester Drawoff							
West-Southwest	128	1750	1340	478	264	2190	3290
Calumet	68	703	352	826	98	2570	383
John E. Egan	167	1070	1820	304	165	3570	3510
Hanover Park	55	655	3220	449	236	1510	3730
Primary and Waste Activated Sludge							
North Side	141	826	1042	268	240	1700	2980
Lemont	25	57	725	506	91	4470	2080
O'Hare	124	888	1542	235	117	2990	2000
Stored Sludge							
Lagoon	252	28	1791	1080	404	4120	6810
Sludge Applied at Fulton County	140	1890	1140	560	300	2380	4610

TABLE 10. Occurrence of organic priority pollutants in digested sludges at district treatment facilities (over period of June through September 1984).

Pollutant	Concentration Range ppb Major Facilities	 Smaller Facilities
Volatiles (Purgeables)		
Chloromethane	nd to 5	nd to 29
Vinyl Chloride	nd to 6	nd to 20
Dichloromethane	nd to 1	nd to 4
1,1-Dichloroethane	nd to 9	nd to 2
trans-1,2-dichloroethene	nd to 7	2 to 3
Chloroform	nd to 12	nd
Trichloroethene	nd to 2	nd
Benzene	nd to 6	nd
Tetrachloroethane	nd to 3	nd
Toluene	61 to 1,291	24 to 1,250
Chlorobenzene	nd to 12	2 to 5
Ethylbenzene	nd to 35	nd to 4
Acid Extractables		
Phenol	nd to 717	nd to 27
2,4-Dimethyphenol	nd to 13	nd
2,4-Dichlorophenol	nd	nd to 10
Base/Neutral Extractables		
1,4-Dichlorobenzene	nd to 36	nd to 16
N-Nitrosodi-n-propylamine	nd to 20	nd
Nitrobenzene	nd to 42	nd
Isophorone	nd	nd to 19

nd = NOT DETECTED
Major facilities include Calumet and West-Southwest Sewage Treatment Works.
Smaller facilities include John E. Egan and Hanover Park Water Reclamation Plants.

TABLE 10. Continued.

Pollutant	Concentration Range ppb Major Facilities	Smaller Facilities
Naphthalene	nd to 103	nd to 28
Acenaphthene	nd	nd to 14
Fluorene	nd to 27	nd to 24
Diethylphthalate	nd to 37	nd to 56
4-chlorophenyl phenylether	nd	nd to 1
4-Nitrosodiphenylamine	nd	nd to 46
Phenanthrene	nd to 91	nd to 92
Anthracene	nd to 44	nd to 26
D-n-Butylphthalate	nd to 22	nd to 39
Fluoranthene	nd to 106	nd to 88
Pyrene	nd to 89	nd to 50
Butyl benzyl phthalate	nd	nd to 66
Benzo(a)anthracene	nd to 53	nd to 30
Chrysene	nd to 75	nd to 48
Bis(2-ethylhexyl)-phthalate	nd to 128	13 to 8,526
Di-n-octylphthalate	nd	nd to 494
Benzo(b)fluoranthene	nd to 78	nd to 58
Benzo(k)fluroanthene	nd to 69	nd to 17
Benzo(a)pyrene	nd to 305	nd to 118
Indeno(1,2,3-cd)pyrene	nd to 34	nd
Pesticides		
Lindane	nd to 6	nd
Heptachlor Epoxide	nd to 6	nd

nd = NOT DETECTED
Major facilities include Calumet and West-Southwest Sewage Treatment Works. Smaller facilities include John E. Egan and Hanover Park Water Reclamation Plants.

TABLE 11. Occurrence of organic priority pollutants in waste-activated sludge at district treatment facilities (over period of June through September 1984).

Pollutant	Concentration Range ppb Major Facility	Smaller Facility
Volatiles (Purgeables)		
Dichloromethane	0.6 to 4.3	0.5 to 1.1
1.1-Dichloroethane	2.1 to 9.5	nd
Trans-1,2-Dichloroethene	nd to 1.5	nd
Chloroform	1.1 to 2.6	nd
1,1,1-Trichloroethane	6.3 to 13.8	nd
Trichloroethene	6.2 to 9.1	nd
Tetrachloroethene	6.8 to 9.5	nd
Toluene	1.6 to 15.8	nd to 1.0
Base/Neutral Extractables		
1,2-Dichlorobenzene	nd to 12	nd to 0.5
Diethylphthalate	nd to 104	nd to 40
4-Bromophenyl phenyl ether	nd	nd to 1
Phenanthrene	nd to 27	nd
Fluoranthrene	nd to 48	nd to 12
Pyrene	nd to 6	nd to 12
Butyl benzyl phthalate	nd to 16	nd
Benzo(a)anthracene	nd to 24	nd
Chrysene	nd to 20	nd
Bis(2-ethylhexyl)phthalate	188 to 1,032	156 to 235
Benzo(b)fluroanthene	nd to 64	nd
Benzo(k)fluoranthene	nd to 40	nd
Pesticides		
Lindane	nd to 6	nd

nd = NOT DETECTED
Major facility is North Side Sewage Treatment Works.
Smaller facility is O'Hare Water Reclamation Plant.

TABLE 12. PCB content of sludges at district treatment facilities during 1983 and 1984.

Sample Source	PCB Content in mg/kg* 1983	1984
John E. Egan Digester Draw	0.076	0.023
Hanover Park Digester Draw	0.021	0.016
Lemont Digester Draw	<0.001	0.014
Calumet Digester Draw	0.167	0.147
West-Southwest Digester Draw	0.128	0.102
O'Hare Return Activated	<0.001	0.006
North Side Waste Activated	0.014	0.012

*Average of four samples each year. Concentrations based on sample as received.

Since the 1960s, concern about the fate of sludge-borne metals has stimulated a large amount of research.

When municipal sludge is applied to soils, the metal content of the soil can be raised in proportion to the metal content of the applied sludge. Table 13 presents data on the concentration of metals in soil at the District's Fulton County site. As expected, sludge application raised the metal content of the surface soil in proportion to the sludge application rate. However, the metal concentrations decreased with soil depth due to the strong affinity of the soil for the metals.

Although the fate of sludge-borne metals in soils is a consideration, of greater interest are the levels of metals in the plants grown on these soils. In general, it has been found that most of the metals are either not taken up by plants or are not a significant public health problem. This statement cannot be made for cadmium, which has been found to be readily taken up by plants and is believed, by some, to present a hazard to human health.

The District has made a considerable effort to determine the levels of metals present in the foodstuffs produced at its land application site. Table 14 contains data on the concentration of metals in sludge fertilized corn produced at the District's Fulton County site. The sludge application significantly raised the concentration of cadmium in the corn grain produced at the Fulton County site.

Existing federal regulations (40 CFR 257) require municipalities who own and operate sludge application to land sites to either limit total and cumulative sludge application or restrict the use of the agricultural products produced to animal feed markets. The District has elected to sell corn grain produced at its Fulton County site to nearby animal feedlots.

TABLE 13. Metals analysis of soil at selected depths from sludge-amended minesoil at the Fulton County site in 1983.

Sludge Application, Dry Solids											
Annual		Cumulative		Soil Depth		Zn	Cd	Cu	Cr	Ni	Pb
Mg/ha	(tons/acre)	Mg/ha	(tons/acre)	cm		mg/kg					
0.0	(0.0)	0.0	(0.0)	0-15		28.1	2.33	14.3	5.30	7.57	9.56
17.9	(8.0)	146.4	(65.3)			118	8.92	50.6	20.7	15.2	31.7
35.9	(16.0)	292.7	(130.5)			269	20.1	106	52.7	24.9	65.8
71.7	(32.0)	585.4	(261.1)			533	39.7	205	108	44.8	110
					LSD†	98.1**	7.58**	37.0**	25.3**	8.62**	20.6**
0.0	(0.0)	0.0	(0.0)	15-30		3.51	0.52	5.94	0.71	4.99	3.30
17.9	(8.0)	146.4	(65.3)			13.1	1.16	7.74	2.21	5.88	4.98
35.9	(16.0)	292.7	(130.5)			26.3	2.12	12.5	5.58	7.72	8.73
71.7	(32.0)	585.4	(261.1)			39.3	3.14	18.5	6.72	8.42	11.8
					LSD†	13.8**	1.14**	6.67**	2.78**	N.S.	4.98*
0.0	(0.0)	0.0	(0.0)	30-46		3.33	0.49	5.09	0.97	4.62	2.39
17.9	(8.0)	146.4	(65.3)			6.91	0.61	4.48	0.65	6.58	3.24
35.9	(16.0)	292.7	(130.5)			10.1	0.93	6.15	2.08	6.55	4.14
71.7	(32.0)	585.4	(261.1)			23.9	1.72	11.8	4.11	6.11	7.27
					LSD†	10.5**	0.78*	4.41*	1.76*	N.S.	2.86*
0.0	(0.0)	0.0	(0.0)	61-76		3.82	0.47	4.68	1.11	6.08	4.10
17.9	(8.0)	146.4	(65.3)			7.82	0.73	5.03	1.17	6.35	3.81
35.9	(16.0)	292.7	(130.5)			10.1	0.95	6.24	1.71	5.41	3.82
71.7	(32.0)	585.4	(261.1)			15.7	1.07	7.50	2.69	4.89	5.35
					LSD†	6.38*	N.S.	N.S.	1.08*	N.S.	N.S.

†LSD procedure, least significant difference, was used to compare two treatment means when analysis of variance (ANOVA) was significant at the 0.05* and 0.01** levels. Two means differ significantly when the difference between them exceeds the LSD value.

N.S. = Not statistically significant.

TABLE 14. Metals analysis of corn grain from sludge-amended minesoil at the Fulton County site for 1983.

Sludge Application, Dry Solids Annual		Cumulative		Zn	Cd	Cu	Cr	Ni	Pb
Mg/ha	(tons/acre)	Mg/ha	(tons/acre)	mg/kg (oven dried, 65°C)					
0.0	(0)	0.0	(0)	30.3	0.14	2.7	1.9	0.68	0.10
17.9	(8)	164.2	(73)	35.6	0.30	2.6	2.1	0.82	0.15
35.9	(16)	328.5	(146)	43.0	0.58	2.6	2.1	1.28	0.12
71.7	(32)	657.0	(293)	50.0	1.06	2.4	2.1	2.30	0.12
			LSD†	3.2**	0.29**	N.S.	N.S.	0.29**	N.S.

†LSD procedure, least significant difference, was used to compare two treatment means when analysis of variance (ANOVA) was significant at the 0.05* and 0.01** levels. Two means differ significantly when the difference between them exceeds the LSD value.

N.S. = Not statistically significant.

Surface and Groundwater

There is the remote possibility that metals in sludge applied to land could migrate to surface and groundwater. However, this is only possible when the sludge or applied soil is carried away through erosion to nearby streams or through cracks and fissures in soils to the groundwater. Selection of suitable sites for land application of sludge and sound management practices will eliminate any possibility of such an occurrence.

The District, at its Fulton County site, has conducted extensive monitoring of the groundwater and surface water. Tables 15 and 16 present metal data for a groundwater monitoring well and surface water site in sludge application areas at the Fulton County site. The tables contain the annual average metal concentrations for 1972 through 1983, annual number of samples collected, and the number of these samples which were above the applicable analytical detection limit.

Table 15 shows that the groundwater metal concentration has not changed for the 11-year period from 1972 to 1983. In fact, it appears that metal concentrations have decreased since sludge application began in 1972.

Table 16 shows the metal concentrations present at a surface water site at the Fulton County site. As for the groundwater, surface water metal concentrations show no effect due to sludge application since 1972.

Earthworms

Earthworms in soils receiving sewage sludge are important in soil processes (Miller 1974) and are useful biological indicators of soil metal availability (Van Hook 1974). Helmke et al. (1979) and Hartenstein et al. (1980) reported that earthworms on sludge-amended soils can accumulate high concentrations of metals, which may pose a potential hazard to the worms and their predators.

The District, at its Fulton County site, has been applying anaerobically digested sewage sludge continually since 1972 to calcareous strip mine spoil. From 1975 to 1977, a study was conducted to determine the accumulations of heavy metals by earthworms in selected minesoil and nonmined fields receiving sewage sludge.

Earthworm metal concentrations observed in selected nonamended and sludge-amended fields are shown in Table 17. Earthworm metal levels ranged from 19 to 506 mg Zn/kg, 0.6 to 98 mg Cd/kg, 0.1 to 8.8 mg Cr/kg, 1.1 to 25 mg Cu/kg, <0.1 to 10 mg Ni/kg, and <0.01 to 2.4 mg Pb/kg.

Metal enrichment ratios (concentration in worms/concentration in soil) for earthworms, at the Fulton County site, are shown in Table 18. The mean enrichment ratios for metals, obtained by dividing the earthworm/soil metal ratio on a sludge-amended field by the ratio on a nonamended field of the same land type for each sampling, indicate that the order of metal accumulation by earthworms in the sludge-amended fields at the Fulton County site was Cu>Cd>Ni>Cr>Pb>Zn.

The metal concentrations in soil and earthworms from nonamended and sludge-amended fields at the Fulton County site were comparable to those found in control and sludge-treated fields of other studies (Andersen 1979; Beyer et al.

TABLE 15. Metal concentration in groundwater within an area which received sewage sludge for twelve years at Fulton County, Illinois.

Groundwater Source		Parameters	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
Well #14	Zn	Mean (mg/L)	13.9	15.2	9.0	14.7	11.8	7.5	8.7	4.6	0.5	0.7	0.6	5.0
		N	11	12	9	11	12	11	9	11	12	12	12	12
		N-Positive	11	12	9	11	12	11	9	11	12	12	12	12
	Cd	Mean (mg/L)	0.005	0.008	0.001	0.004	0.008	0.002	0.000	0.012	0.008	0.009	0.008	0.005
		N	11	12	9	11	12	11	9	11	12	12	12	12
		N-Positive	2	6	1	3	2	1	0	6	3	5	5	3
	Cu	Mean (mg/L)	0.08	0.02	0.01	0.09	0.02	0.02	0.01	0.01	0.02	0.00	0.01	0.01
		N	11	12	9	11	12	11	9	11	12	12	12	12
		N-Positive	10	5	3	11	8	6	3	5	1	0	5	4
	Ni	Mean (mg/L)	0.06	0.13	0.01	0.02	0.00	0.02	0.01	0.05	0.08	0.01	0.08	0.06
		N	11	12	9	11	12	11	9	11	12	12	12	12
		N-Positive	4	4	1	1	0	1	1	5	6	1	6	7
	Pb	Mean (mg/L)	0.08	0.17	0.21	0.20	0.10	0.07	0.10	0.07	0.04	0.01	0.01	0.00
		N	11	12	9	11	12	11	9	11	12	12	12	12
		N-Positive	7	10	9	11	11	8	8	7	4	4	3	0

N-Number of samples.
N-Positive is the number of samples with metal concentration above the detection limits which were: Zn 0.1, Cd 0.02, Cu 0.02, Ni 0.1, and Pb 0.02 mg/L.

TABLE 16. Metal concentration in surface water within an area which received sewage sludge for twelve years at Fulton County, Illinois.

Surface Water Source		Parameters	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983
Reservoir #3	Zn	Mean (mg/L)	0.05	0.0	0.0	0.00	0.00	<0.1	0.008	0.033	0.025	0.017	0.000	0.033
		N	12	12	12	12	12	11	12	12	12	12	3	3
		N-Positive	4	0	0	0	1	0	1	3	3	1	0	1
	Cd	Mean (mg/L)	0.005	0.000	0.000	0.000	0.000	<0.01	0.001	0.003	0.000	0.003	0.00	0.000
		N	12	12	12	12	12	12	12	12	12	12	3	3
		N-Positive	4	1	0	0	1	0	1	3	0	1	0	0
	Cu	Mean (mg/L)	0.083	0.01	0.02	0.01	0.08	0.07	0.007	0.003	0.002	0.002	0.007	0.033
		N	12	12	12	12	12	12	12	12	12	12	3	3
		N-Positive	7	7	5	3	12	10	3	3	1	1	1	1
	Ni	Mean (mg/L)	0.049	0.00	0.0	0.02	0.00	<0.1	0.008	0.042	0.050	0.058	0.10	0.000
		N	12	12	12	12	12	12	12	12	12	12	3	3
		N-Positive	2	0	0	1	0	0	1	5	4	6	3	0
	Pb	Mean (mg/L)	0.09	0.06	0.07	0.02	0.02	0.04	0.026	0.065	0.017	0.010	0.023	0.013
		N	12	12	12	12	12	12	12	12	12	12	3	3
		N-Positive	5	8	11	6	8	8	6	8	2	3	2	2

N-Number of samples.
N-Positive is the number of samples with metal concentration above the detection limits which were: Zn 0.1, Cd 0.02, Cu 0.02, Ni 0.1, and Pb 0.02 mg/L.

TABLE. 17. Metal concentrations in soils and earthworms at the Fulton County land reclamation site. (continued on p. 124)

Land Type	Metal	Sample Type	Nonamended	Sludge Amended†
			mg/kg dry wt.	
Minesoil	Zn	Soil	50±11 (40-68)‡	78±19 (66-98)
		Earthworms	174±106 (33-293)	231±157 (19-436)
Minesoil	Cd	Soil	0.6±0.4 (0.3-1.3)	2.0±1.4 (0.6-4.0)
		Earthworms	3.8±3.3 (0.6-9.1)	22±19 (3.0-57)
Minesoil	Cr	Soil	23±1.5 (21-25)	38±11 (24-51)
		Earthworms	1.2±1.2 (0.1-2.8)	2.3±2.6 (0.3-7.0)
Minesoil	Cu	Soil	22±2.5 (18-25)	36±3.7 (32-41)
		Earthworms	7.0±5.2 (1.1-15)	10±4.9 (5.4-16)
Minesoil	Ni	Soil	40±10 (29-53)	57±13 (37-77)
		Earthworms	3.2±3.4 (<0.1-8.4)	3.2±3.6 (0.7-10)
Minesoil	Pb	Soil	13±1.0 (12-14)	18±6.7 (8.8-27)
		Earthworms	0.44±0.79 (<0.01-2.0)	0.50±1.0 (<0.01-2.4)

†Cumulative amounts of sewage sludge applied to two fields representative of minesoil and nonmined lands were 174 and 188 Mg ha^{-1} dry solids, respectively.

‡Mean, standard deviation, and range for six samplings during 1975-1977.

TABLE 17. Continued.

Land Type	Metal	Sample Type	Nonamended	Sludge Amended†
			mg/kg dry wt.	
Nonmined	Zn	Soil Earthworms	72±18 (49-94) 264±153 (68-439)	87±34 (49-130) 329±218 (46-506)
Nonmined	Cd	Soil Earthworms	1.0±0.4 (0.6-1.6) 12±8.1 (1.6-21)	3.5±1.8 (1.3-5.4) 36±35 (3.8-98)
Nonmined	Cr	Soil Earthworms	18±3.5 (12-22) 0.6±0.4 (0.1-1.1)	45±20 (24-73) 2.6±3.2 (0.2-8.8)
Nonmined	Cu	Soil Earthworms	24±6.8 (20-38) 6.4±3.7 (1.4-9.8)	33±11 (20-47) 11±8.3 (2.1-25)
Nonmined	Ni	Soil Earthworms	36±6.0 (29-44) 1.2±0.8 (<0.1-2.2)	35±3.4 (30-37) 2.8±2.5 (<0.1-6.0)
Nonmined	Pb	Soil Earthworms	18±3.1 (14-22) 0.20±0.32 (<0.01-0.82)	28±6.1 (21-38) 0.55±0.78 (<0.01-2.0)

† Cumulative amounts of sewage sludge applied to two fields representative of minesoil and nonmined lands were 174 and 188 Mg ha^{-1} dry solids, respectively.

‡Mean, standard deviation, and range for six samplings during 1975-1977.

TABLE 18. Metal enrichment ratios in earthworms at the Fulton County land reclamation site.

	Earthworm Metal Enrichment Ratios[†]			
	Minesoil		Nonmined	
Metal	Nonamended	Amended	Nonamended	Amended
Zn	3.5±2.0[‡]	3.1±2.1	3.8±2.3	4.3±3.7
Cd	8.0±6.6	19±19	15±12	21±30
Cr	0.05±0.05	0.08±0.11	0.04±0.02	0.06±0.05
Cu	0.10±0.10	0.43±0.31	0.28±0.18	0.33±0.21
Ni	0.09±0.11	0.07±0.10	0.03±0.02	0.08±0.07
Pb	0.03±0.06	0.05±0.11	0.01±0.01	0.02±0.03

[†] Earthworm metal concentration, mg/kg + soil metal concentration, mg/kg, for the six sampling dates.

[‡] Mean ration ± standard deviation.

1982; Helmke et al. 1979). Pietz et al. (1984) reported that the soil metal concentrations observed at the Fulton County site were certainly not toxic to worms. However, little is known about the actual impact of biologically accumulated metals on earthworm predators in terrestrial systems.

Chickens

Research has shown that Zn and Cd are the two metals with the greatest bioaccumulation in crops grown on sludge-amended lands. Of these two metals, Cd is considered, by some, to present the greatest potential hazard to animal health. Chickens are consumers of feed grains, which can come from sludge-amended soils, and chickens consume more feed per unit of body weight than other animals.

Hinesly et al. (1984) examined the responses of white leghorn chickens to biologically accumulated Cd in formulated corn and soybean grain feed rations grown on sewage sludge-amended strip-mined land at the District's Fulton County site. Selected groups of pullet chicks were fed low-, medium-, and high-Cd diets containing 0.095, 0.567, and 0.966 mg Cd/kg, respectively, made from these feed grains.

Cadmium concentrations in egg constituents at various intervals during the study are shown in Table 19. Hinesly et al. (1984) reported that the Cd concentrations in the various egg constituents did not vary significantly, and that the egg whites and yolks generally contained Cd levels that were below the detection limits of 0.062 mg/kg. They also reported that the amounts of Cd in egg shells increased with the age of the hens, but the shell-Cd levels were not affected by the Cd levels in the diets. Leach et al. (1979) using $CdSO_4 \cdot 8H_2O$, also found that the transfer of dietary Cd to eggs was very low.

Analyses of various tissues in the hens 50 weeks after hatching for selected metals are shown in Table 20. Concentrations of Cd in the gizzard, gizzard lining, kidney, leg muscle, and liver were significantly increased by higher Cd levels in the diets. Although Cd levels were elevated in selected tissue of laying hens after 50 weeks (Table 20), Hinesly et al. (1984) concluded that the levels of Cd in soybean and corn grain grown on sludge amended soils was not a significant hazard to the human food chain.

Damron et al. (1981) in feeding corn grown on sludge-amended plots to hens and broilers, reported that metal levels in the liver, kidney, and muscle tissues were not influenced by dietary treatment. Underwood (1977) reported that 5 mg Cd/kg diet usually is required to produce adverse physiological effects in animals with an adequate diet. The Cd levels in rations fed to laying hens by Hinesly et al. (1984) were considerably less than the 5 mg Cd/kg diet reported by Underwood (1977). This indicates that the conclusions by Hinesly et al. (1984) on the use of food grains from sludge-amended lands for poultry rations are realistic.

Cattle

Bioaccumulation of sewage sludge-applied metals in livestock has been an area of considerable interest for several years. Heavy metals biologically incorporated into plant material which is used as animal feed affect animals much differently than heavy metal salts that are force-fed to animals. (Shaikh and Lucis 1972; Syverson 1975). Studies that have used metal salts consistently show much higher metal accumulations in animal tissues than studies using plants actually grown on sludge-amended soils.

At the District's Fulton County site, cattle were allowed to graze for up to eight years on pastures amended with anaerobically digested sewage sludge. The objective of this study, reported by Fitzgerald et al. (1985) was to determine the degree of metal accumulation in tissues of cattle chronically exposed to sewage sludge.

Fitzgerald et al. (1985) reported that cows in both the control and test herds appeared to calve normally without complications. Metal concentrations in tissues of adult cows during the eight year study are shown in Table 21. The metals Zn, Cu, and Cd increased most consistently in the liver and kidney of cows in the test herd. The concentrations of these metals in liver tissue from the test herd were about 2.1, 0.6, and 7.7 times higher, respectively, than those of the control herd. In the kidneys, Cd concentrations were the same in both herds, while Zn and Cd were 1.2 and 4.9 times higher, respectively, in the test herd.

TABLE 19. Mean cadmium concentrations in egg constituents sampled at various intervals during a 54-week period commencing when egg laying began.

Number of Weeks After Laying Began	Cd Treatment	White	Yolk	Shell
		---mg/kg dry wt.---		
6	Low	<0.062	<0.062	0.114
	Medium	<0.062	<0.062	0.149
	High	<0.062	<0.062	0.148
	F-test[†]	n.s.[‡]	n.s.	n.s.
15	Low	<0.062	0.068	0.068
	Medium	<0.062	<0.062	0.071
	High	<0.062	0.111	0.090
	F-test	n.s.	n.s.	n.s.
24	Low	<0.062	<0.062	0.101
	Medium	<0.062	<0.062	0.124
	High	<0.062	<0.062	0.088
	F-test	n.s.	n.s.	n.s.
32	Low	<0.062	<0.062	0.352
	Medium	<0.062	<0.062	0.365
	High	<0.062	<0.062	0.294
	F-test	n.s.	n.s.	n.s.
41	Low	0.317	<0.062	0.456
	Medium	0.144	<0.062	0.320
	High	0.125	<0.062	0.340
	F-test	n.s.	n.s.	n.s.
54	Low	<0.062	<0.062	0.303
	Medium	<0.062	<0.062	0.325
	High	<0.062	<0.062	0.347
	F-test	n.s.	n.s.	n.s.

[†] Analysis of variance.

[‡] Nonsignificant F-test.

TABLE 20. Concentrations of metals in various tissues of hens fed low-, medium-, and high-cadmium diets formulated from corn and soybeans grown on sludge amended soil.†

Diet	Metals					
	Zn	Cd	Cu	Mn	Fe	Pb
	mg/kg fat-free dry wt.					
			Breast Muscle			
Low	18.8	0.134	1.20	0.136	15.1	<0.62
Medium	19.4	0.0948	1.22	0.345	12.9	<0.62
High	21.0	0.112	1.51	0.422	21.3	<0.62
LSD	n.s.‡	n.s.	n.s.	n.s.	n.s.	n.s.
			Gizzard			
Low	128	1.03	4.55	3.84	186	0.85
Medium	125	4.27	4.80	3.40	181	<0.62
High	132	9.34	5.42	3.78	188	0.65
LSD	n.s.	3.33*	n.s.	n.s.	n.s.	n.s.
			Gizzard Lining			
Low	22.5	1.39	33.4	21.7	85.8	1.12
Medium	24.7	8.78	35.8	18.5	93.9	1.45
High	29.7	13.6	56.0	28.2	74.6	1.73
LSD	n.s.	5.79**	13.2*	n.s.	n.s.	n.s.
			Kidney			
Low	118	4.61	12.9	10.1	359	<0.62
Medium	125	21.8	13.1	11.6	382	<0.62
High	142	36.8	13.8	13.2	330	<0.62
LSD	n.s.	4.8**	n.s.	2.4**	n.s.	n.s.
			Leg Muscle			
Low	116	0.111	4.05	0.874	81.0	0.83
Medium	118	0.163	3.70	0.762	64.0	<0.62
High	108	0.110	4.06	0.760	62.0	<0.62
LSD	n.s.	0.039*	n.s.	n.s.	n.s.	n.s.
			Liver			
Low	128	0.898	16.0	9.40	337	0.99
Medium	138	3.57	14.7	13.0	303	<0.62
High	134	6.18	16.2	11.9	257	<0.62
LSD	n.s.	0.190**	n.s.	n.s.	n.s.	n.s.

*, **Significant at 0.05 and 0.01 levels, respectively.

†Samples taken 50 weeks after hatching.

‡Nonsignificant F-test.

LSD-Least significant difference.

TABLE 21. Heavy metals in tissues of adult cows ingesting forage treated with anaerobically digested sewage sludge between 1973 to 1980.

Tissue	Metals						
	Zn	Cu	Cd	Cr	Ni	Pb	Fe
	mg/kg dry wt.						
Diaphragm							
Exp (63)†	116	5	0.076	0.206	0.234	0.1	97 (40)†
Cont (29)	125	5	0.036	0.215	0.506	0.1	109 (20)
Heart							
Exp (64)	60	15	0.159	0.172	0.391	0.1	196 (40)
Cont (28)	60	15	0.050	0.434	0.279	0.1	193 (19)
Liver							
Exp (64)	163	162	7.721	0.186	0.184	0.1	169 (40)
Cont (28)	104	78	1.086	0.365	0.148	0.1	148 (20)
Kidney							
Exp (64)	104	19	43.800	0.231	0.499	0.1	270 (40)
Cont (28)	85	19	8.869	0.390	0.272	0.1	261 (20)
Brain							
Exp (59)	43	12	0.055	0.209	0.321	0.1	95 (40)
Cont (24)	40	10	0.032	0.306	0.587	0.1	98 (18)
Bone							
Exp (62)	49	1.5	0.064	0.614	0.702	1.8	10 (40)
Cont (27)	57	1.2	0.245	0.934	1.181	0.6	8 (19)
Blood (wet weight)							
Exp (78)	3.1	1.0	0.002	0.025	0.007	0.086	ND‡
Cont (18)	3.0	1.0	0.004	0.010	0.009	0.022	ND
Milk (wet weight)							
Exp (16)	2.94	0.14	0.003	0.248	0.086	0.013	ND
Cont (5)	2.53	0.13	0.002	0.160	0.050	0.010	ND

†Notations designate numbers of cows from which tissue samples were obtained in experimental and control herds, respectively.
‡Not determined.

Although the concentrations of Zn, Cu, and Cd in the liver and kidney tissues of the experimental herd (Table 21) were higher than those of control cattle, Fitzgerald et al. (1985) reported there was no evidence of disease and tissue lesions in the test herd.

Several other studies have been conducted to evaluate metal retention in cattle ingesting sewage sludge directly or grazing on sludge treated pastures (Baxter et al. 1982; Bertrand et al. 1980, 1981; Smith et al. 1979). Elevations of metals occurred in the liver and kidney, but the metal concentrations were always below tolerable levels established for fish and other food products. These studies also reported that there were no differences between sludge application amounts and animal health performance. Baxter et al. (1982) concluded that cattle can directly consume significant amounts of anaerobically digested sludge or graze on sludge-amended pastures with no apparent negative effects on animal health or performance. In summarizing cattle research, Bertrand et al. (1981) concluded that the "risks to animal health and the human food chain from toxicants in the sewage solids, including heavy metals, were manageable."

Fish

An environmental monitoring program was initiated in 1971 to determine the impact of sludge distribution upon the fish population in lakes and streams within the District's Fulton County site. Changes in the trace metal content of fish tissue, including analysis of concentrations in fish fillets, liver and kidney, were studied to determine the effects of digested sludge application upon lake fish populations within the District site.

Three reservoirs were selected as monitoring sites. Reservoirs R10 and R12 ar both mine-spoil cuts, having become filled with groundwater and rainwater following cessation of former strip-mining operations. R10 is located outside of the sludge distribution watershed. R12 receives runoff from 44 hectares (110 acres) of cropland fertilized with digested sludge. Reservoir R3 is a stream impoundment which receives drainage from 1,600 hectares (3,954 acres), including 216 hectares (533 acres) of sludge fertilized cropland. R3 receives more drainage than any other reservoir on the District site.

Results of the analysis of fish fillets for Zn, Cu, Cd, Cr, and Ni for fish collected from Reservoirs 3, 10, and 12 are listed in Tables 22 and 23.

In general, the mean concentrations of trace metals in the fillets of fish from the three reservoirs exhibited a tendency to decrease over the study period, 1971–1976. Several species, contained significantly higher concentrations of Zn and Cr in 1976 than in 1971/1972.

The mean values for zinc (64 μg/g and 46 μg/g, respectively, for the R3 hybrids and R12 bluegill) from the 1976 collection were much lower than the 500 μg/g (based on dry weight) zinc concentration considered dangerous in fish for human consumption (Murphy et al. 1978; Uthe and Bligh 1971). The maximum concentrations of zinc determined for these fish from R3 (121 μg/g) and R12 (71 μg/g) were well below the 500 μg/g limit. Therefore, these concentrations do not pose a danger to the public health.

Since no sludge application occurred within the watershed of Reservoir 10, the high chromium concentration 547 ng/g in R10 redear sunfish fillets (Table 23) was probably within the natural range of variation for this metal in the muscle tissue of this species.

In summary, the fish study at the Fulton County site shows that metal accumulation in fish tissue is not a problem in water bodies receiving runoff from sludge applied fields. This is expected since very little of any metals are translocated from sludge applied fields unless considerable soil erosion occurs. At well managed sites such soil erosion will not occur.

Summary of Metal Accumulation in Animals

The studies reported above demonstrate that only under very favorable circumstances do metals applied to land, via sludge, accumulate in animal tissues. In many instances such accumulation does not occur. When metals do accumulate, they tend to concentrate in the organs (kidneys, liver) of animals rather than the muscle tissue. Since muscle tissue is the principal source of meat in the human diet, the impact of sludge application on the human diet is minimal since most animals receive their diet from unamended crops. The USEPA (40 CFR 257), in fact, does not limit sludge application to land where the crop is used solely for animal feed.

FATE OF ORGANICS IN MUNICIPAL SLUDGE APPLIED TO LAND

Widespread occurrence of organic compounds such as organo-chlorine pesticides has been reported in agricultural soils in many states of the United States which have never received municipal sludge application. This being the case, it is not surprising that organic compounds are found in municipal sludge-amended soils. District sludge is no exception and does contain various organic compounds (Tables 10, 11, and 12).

There is concern among some environmental engineers, scientists, and agriculturists about the fate of the organics that are placed on land via sludge application. Various possibilities exist for the fate of these compounds in sludge-amended soils. Understanding the possible fate stems primarily from observations made in investigations undertaken to study the fate of PCBs and to a lesser degree, the fate of other organics. The various pathways by which organic compounds are mobilized and/or immobilized are listed in Table 24.

Soils

Information on the adsorptive properties of organics in sludge-amended soils is sparse. However, some information exists on the relative adsorption of PCBs on different soils. The relatively high retention of these compounds by soil appears to be related to their poor solubility in water and to the high adsorptive

TABLE 22. Concentrations of trace metals in fillets of fish sampled from reservoir 3 with results of statistical analyses of the mean values.

Species	Year Collected	Number of Fish	Trace metal, Mean (dry weight) Zn µg/g	Cu µg/g	Cd ng/g	Cr ng/g	Ni ng/g
Largemouth bass	1971/1972	36	40	1.79	13.3	306	362
	1973	14	37	5.87	22.0	523	373
	1974	30	56	0.91	7.7	282	785
	1976	30	44	0.75	12.9	287	456
Difference among means:			**	**	ND	**	ND
Black crappie	1971/1972	15	42	2.54	12.6	353	683
	1974	15	37	0.89	11.8	152	508
	1976	15	31	0.43	11.5	261	540
Difference among means:			**	**	ND	ND	ND
Bluegill	1971/1972	32	63	5.09	109.5	424	3472
	1974	31	47	2.75	101.9	398	1353
	1976	30	53	0.92	6.1	584	872
Difference among means:			**	ND	**	ND	**

* Significant at the 0.05 level.
** Significant at the 0.01 level.
ND = No significant difference.

TABLE 22. Continued.

Species	Year Collected	Number of Fish	Trace metal, Mean (dry weight)				
			Zn µg/g	Cu µg/g	Cd ng/g	Cr ng/g	Ni ng/g
Green sunfish	1971/1972	36	41	4.00	17.4	447	1778
		20	50	1.94	13.0	558	638
		20	42	0.98	9.8	819	883
Difference among means:			**	ND	ND	ND	ND
Green sunfish x bluegill hybrids	1971/1972	25	54	1.84	32.9	425	1087
	1974	29	48	1.21	13.1	238	222
	1976	10	64	1.37	8.6	415	968
Difference among means:			**	ND	**	**	**
Yellow Bullhead	1971/1972	25	43	3.25	86.2	188	345
	1974	25	32	2.58	12.2	155	803
	1976	25	33	1.37	8.7	449	407
Difference among means:			**	**	**	ND	**

* Significant at the 0.05 level.
** Significant at the 0.01 level.
ND = No significant difference.

TABLE 23. Concentrations of trace metals in fillets of fish sampled from reservoirs 10 and 12 with results of statistical analyses of the mean values.

Species	Year Collected	Number of Fish	Trace metal, Mean (dry weight) Zn µg/g	Cu µg/g	Cd ng/g	Cr ng/g	Ni ng/g
R12 Largemouth bass	1971/1972	13	48	2.73	26.5	336	439
	1974	17	57	1.25	27.9	587	2273
	1976	30	37	0.91	13.5	501	758
Difference among means:			**	**	ND	ND	ND
R12 Bluegill	1971/1972	30	40	1.78	74.1	730	825
	1974	31	35	1.86	13.5	653	1010
	1976	30	46	1.29	20.9	519	488
Difference among means:			**	ND	*	ND	*
R10 Largemouth	1971/1972	46	42	2.46	32.7	313	375
	1974	36	52	3.06	17.3	251	246
	1976	30	37	1.19	11.7	331	406
Difference among means:			**	**	*	ND	*

* Significant at the 0.05 level.
** Significant at the 0.01 level.
ND = No significant difference.

TABLE 23. Continued.

Species	Year Collected	Number of Fish	Trace metal, Mean (dry weight)				
			Zn µg/g	Cu µg/g	Cd ng/g	Cr ng/g	Ni ng/g
R10 Green sunfish	1971/1972	20	30	1.72	13.0	329	747
	1974	19	31	2.37	14.1	196	1647
	1976	20	29	0.96	24.7	363	594
Difference among means:			ND	ND	ND	*	*
R10 Redear sunfish	1971/1972	30	38	1.36	34.0	273	486
	1974	25	40	0.50	11.1	143	930
	1976	28	42	0.65	4.4	547	377
Difference among means:			ND	**	ND	**	**
R10 Redear x Green sunfish Hybrids	1971/1972	15	35	1.21	11.5	251	428
	1974	7	41	3.53	5.4	152	437
	1976	18	32	0.84	8.8	259	326
Difference among means:			**	**	ND	ND	ND

* Significant at the 0.05 level.
** Significant at the 0.01 level.
ND = No significant difference.

TABLE 24. Potential fate of organic compounds in sludge-amended soils.

1. Adsorption onto soil and its constituents.
2. Movement to groundwater and to surface waters by runoff.
3. Degradation (Microbial and Photolysis).
4. Volatilization.
5. Uptake by roots and aerial parts of plants.
6. Uptake and accumulation by macro- and microfauna in soil and by birds, animals, etc. that come in contact with sludge-amended soils.
7. Uptake by man either directly or indirectly by consumption of contaminated vegetable matter, fish, milk, meat, and other edible products that are derived either directly or indirectly from the sludge-amended soil environment.

capacity of soil and the associated organic matter. Opportunities for organics to leach into groundwater will be great only if they are highly soluble in water, not amenable to microbial degradation, or are applied at a high concentration on highly porous soils.

Tucker et al. (1975) reported on the relative ease of leaching Arochlor 1016 at a concentration of 2.5% in different soils. This concentration is extremely high for a sludge-amended soil. Tucker et al. (1975) ranked the degree of leaching (highest to lowest) of PCB in soils as sandy loam > silty loam > clay. Despite the high PCB application rates used, less than 0.05 percent was leached from the soil column over a four-month period.

The results of a study by Moza et al. (1976) indicated that only 0.2 percent of the dichlorobiphenyls applied in a 0 to 10 cm soil zone was able to be leached to a depth of 40 cm over a period of two years, thus showing a very high degree of retention by soil. A very high degree of adsorption of PCBs, polybrominated-biphenyls (PBBs), and hexachlorobenzene (HCB), by soils and the associated organic matter was also reported by Griffin and Chou (1981).

Municipal sludge has a very high adsorption capacity for organics. If the adsorbed organics also have a poor solubility in water, it is highly unlikely that the organics applied on land via sludge will be leached by rainfall. Data gathered in 1975 by the District on PCB concentrations in water samples collected from 27 wells located in the Fulton County site indicated that 26 wells did not contain any PCBs, and the other well contained 0.1 ppb. These data were gathered after two years of application of sludge to the surrounding soil. The PCB concentration of the applied sludge ranged from 4.0 to 7.8 ppm.

Davis et al. (1981) applied Milorganite (dried sludge from a sewage treatment plant in Milwaukee, Wisconsin) containing 3.4 ppm of PCBs. They found increasingly higher concentrations of PCBs in the soil over a seventeen-month period and concluded that PCBs were immobilized and remained in the soil.

Baxter et al. (1983) reported the occurrence of PCBs (AR 1254), p-p' DDE, p-p' DDD, chlordane, dieldrin, and p-p' DDT at concentrations of 4,252, 300, 1,535, 86, 497, and < 40 μg/kg in sludge, respectively. In soils amended with this sludge, they detected only the first four compounds listed at a much lower concentration; i.e., < 625 μg/kg, < 25 μg/kg, < 12.5 μg/kg, and < 10 μg/kg of soil. Although these authors did not suggest a possible removal mechanism for these compounds, it is likely that dilution and adsorption was achieved by blending the sludge with soil. Decomposition and volatilization also may be contributing phenomena.

Photodecomposition of specific sludge-borne organic compounds applied to land is possible and depends on the overall ultraviolet radiation available per unit area and the degree of penetration. Pal et al. (1980) reviewed the literature on the photodecomposition of PCBs and found that field data on the rates and magnitude of decomposition of organics is meager. However, it is highly unlikely that photodecomposition of organics incorporated into soil by injection will be a major factor since UV radiation can only penetrate about 1 mm into soil. However, if sludge is applied by spraying and the organics are deposited as a thin layer, either on soil or on vegetation, photodecomposition of the organics is more likely to occur.

Microbial decomposition in the soil of various organics has been studied. The fate of petroleum hydrocarbons in sewage sludge was studied in a land application system (Liu 1980). The results indicated that 77% of the petroleum hydrocarbons were degraded by soil microorganisms in the top 1 cm of soil in about one year. He also noted a rapid decrease in organic concentration in silt loam with depth (26.1 mg/g soil at 0–1 cm to 1.8 mg/g at 3–4 cm, and 0.7 mg/g at 6–7 cm) and suggested that this type of soil has the ability to degrade as well as retain the petroleum hydrocarbons.

The decomposition rates of organic compounds by soil microorganisms are likely to be affected by synergistic and antagonistic relationships among the organic compounds and the microorganisms present in a land application system. Hence, the degradation rates of specific organic compounds may widely vary at sludge application sites.

Losses of organic compounds present in sludge applied to land are possible via volatilization. Such volatilization losses depend on the concentration of the compound in the sludge-soil system, vapor pressure of the compound, temperature, soil water content, adsorptive properties of the concerned compound and air movement (Spencer et al. 1973).

Information on losses of organics due to volatilization occurring in sludge-amended soils is sparse. The volatilization half-lives of Arochlor 1221 and Arochlor 1016 were reported to be 12 and 15 days in activated sludge (Tucker et al. 1975).

Potential volatilization rates of lindane, dieldrin, and DDT were reported by Farmer et al. (1972). Their data indicate that volatilization rates of these compounds increase with an increase in the soil concentration and in the air velocity over the soil surface. They also found that the volatilization rate of pesticides applied on soil decreases with time.

Moza et al. (1976) have reported high volatilization losses of trichlorobiphenyl and pentachlorobiphenyl from soil on which beets and carrots were grown. The losses for these compounds were 67.5 and 41.5%, respectively. Less than 2% of these compounds were apparently converted to other intermediate products.

In general, the data sited above show that the soil has a very high affinity for the organics contained in municipal sludge. Organics are tightly held by the soil and are not leached from the soil. Carryover to surface and groundwater is only possible if erosion of soil particles occurs. Therefore, like the metals, the organics in sludge pose no hazard to surface and groundwater at well-managed, sludge-amended land sites.

Plants

The uptake of organic compounds contained in sludge by roots and aerial parts of vegetation growing on sludge-amended soils is of concern because of the potential health hazard that might occur due to the concentration of such compounds in the components of the food chain. Only water soluble organic compounds can be readily taken up by plants. Depending on the concentration of organics in the water phase, the organics could translocate into plant tissue or possibly exert phytotoxicity. On the other hand, some organics can actually stimulate plant growth at very low concentrations. In some instances, it is even possible for the organic compound to degrade within the plant or even migrate back to the roots and soil (Overcash, 1983).

While some researchers have detected plant uptake of organics from sludge applied to land, others have not. Baxter et al. (1983) in studies using sludge from the Denver sewage treatment facility, reported that none of the organics present in the sludge were taken up by plants. Plants grown on land amended with sludge containing 2,000 ppm of di-n-phthalate accumulated very little of this compound (Shea et al. 1982). Iwata et al. (1974) reported the translocation of PCBs into carrots from a soil into which 100 ppm of Arochlor 1254 were applied to a depth of 6 inches. The highly chlorinated PCBs were not degraded in soil, whereas PCBs with a lower degree of chlorination were dissipated to some extent. Highly chlorinated PCBs, however, were taken up to a greater degree by the carrots than were PCBs with a lower degree of chlorination. About 97% of the applied PCBs were translocated due to their lipophilic nature into the peel of the carrots, which contains a high fat content. Linseed also takes up PCBs because of its high fat content (Finlayson and McCarthy 1973; Nash 1974).

Moza et al. (1979) speculated that spruce trees and other coniferous trees may accumulate the lipophilic PCBs as they contain oils in the plant tissue. However, they reported that in studies conducted with forest soils amended with sludge, only 0.8% of the PCBs contained in the applied sludge was translocated into the spruce trees. Less than 0.1% of the PCBs was detected in the leachate in the first 2 years after sludge was applied and none was detected after the 2 years. These authors concluded that spruce trees cannot possibly act as a major sink for PCBs applied on land via sludge.

The translocation and accumulation of lipophilic organics in other root crops such as beets, onions, turnips, and rutabagas is much lower than in carrots, due to a considerably lower concentration of lipids in these root crops (Iwata et al. 1974; Fox et al. 1964; Lichtenstein et al. 1965).

Based on the results discussed above, it is reasonable to conclude that translocation and uptake of organics into plant tissues play a very minor role in determining the fate of organics applied via sludge onto land.

Animals and Insects

A few studies have been reported on the uptake of organics by insects and animals when they are exposed to sludge-amended soils and/or when they consume feed stuffs derived from such soils. Davis et al. (1981) reported PCB biomagnification factors of 1.3 (i.e., 1.3 times the PCB concentration in soil) and 0.8 for primary consumers such as arthropods and secondary consumers such as spiders, lady bugs, etc., inhabiting a soil which was amended with Milorganite. Fitzgerald (1981) noted higher levels of PCB in visceral fat of cows pastured on land amended with District sludge than the fat of control animals.

Baxter et al. (1985) examined fat, liver, kidney, muscle, bone, brain, lung, spleen, and blood of 12 experimental cows that were kept on a sludge application site and compared the results with those obtained from an examination of similar tissues obtained from 6 cows kept as controls. They found hexachlorobenzene, benzene hexachloride, p-p'DDE, dieldrin, and Arochlor-1254 at comparable levels in both groups of animals and concluded that there was little accumulation of the refractory organics in the tissues of animals exposed to sludge-amended soils. These authors also conducted experiments with cattle to determine whether persistent organics contained in sludge would accumulate in the tissues of animals, which were fed sludge as a diet supplement. They reported that significantly higher concentration of some organics were detected in the fat of the animals than in the fat of animals that were put on a control diet. However, all the observed concentrations of the organics in the control and experimental animals were less than the tolerence levels established by the Food and Drug Administration for fish and other food products. An increase in the concentration of refractory organics was also reported by Kienholz (1980) in beef cattle when they were fed a diet supplemented with 12% sewage sludge for a period of 94 days. Sheep and guinea pigs also showed an increase in liver PCB concentration when cabbage grown on sludge-amended soil was fed to them (Hansen and Chaney 1981).

The fatty tissues of sows overwintered for two seasons on plots which received District sludge at various loading rates, were examined by Hansen et al. (1981) for various pesticides and PCBs. Only PCBs and p-p'DDE accumulated in the fatty tissue of sows in proportion to the sludge application rate.

Fries (1982) discussed the uptake of organics contained in municipal sludge applied to land by animals. The pathways of uptake found included direct ingestion of sewage sludge adhering to forage and other vegetation, uptake by indirect contamination or volatilization and subsequent adsorption, and the ingestion of contaminated soil while grazing. Ingestion of contaminated soil was suggested to be the most significant pathway for PCB uptake by animals in comparison to others. Fries (1982) stated that the concentration of PCB in lactating animals may be four to five times the PCB concentration in the diet of the animals. The milk fat PCB concentration could be 0.7 ppm for each ppm of PCB in soil when cows consume contaminated soil along with forage. However, by a careful choice of dietary supplementation and good management techniques of sludge applications and grazing schedules, the milk fat PCB concentration could be reduced to about 0.25 ppm for each ppm of PCB in sludge, which is far less than the tolerance limit of PCB set by the Food and Drug Administration for milk.

Because of the concern about possible PCB contamination of milk by animals grazing on sludge-amended soils where the sludge is not incorporated, the USEPA currently limits (40 CFR 257) the PCB content of the applied sludge to 10 ppm or less. Since most municipal sludges have PCB levels much below 10 ppm, compliance with this restriction is relatively easy. In any event, if the sludge is incorporated, there is no possibility of sludge ingestion by the grazing animals and the restriction on sludge PCB content does not apply.

Humans

No data are available on the literature which related to the effects of organics in sludge on humans. However, an incident was reported in the scientific literature regarding the health of individuals exposed to vegetables fertilized with a high PCB content municipal sludge.

In the March 24, 1978 issue of the Center for Disease Control (CDC) Morbidity and Mortality Weekly Report (Volume 27, Number 12), a case was presented where a municipal sludge from around Bloomington, Indiana, high in PCB—averaging 479.1 ppm of PCB and ranging up to 1,700 ppm—was used by the general public as a garden fertilizer. Soil samples from gardens showed an average PCB concentration of 17.1 ppm, and a maximum of 107 ppm. To evaluate the possible health effects of PCB exposure, the local board of health and CDC conducted epidemiological and clinical observations of the exposed population. The conclusions of the clinical evaluations were:

1. Blood serum levels of PCB of residents exposed to the sludge were found not to be significantly different from those not exposed;
2. Blood serum PCB levels showed no correlation with the number of years sludge was used as a fertilizer, total pounds of sludge used, or the interval since last use; and
3. No evidence was found to indicate that exposure to PCB contaminated sludge applied as a fertilizer resulted in increased adsorption of PCB.

Summary of Fate of Organics Information

The data on the public health effects of organics in sludge applied to land is meager. However, there have been some studies done, principally related to the PCB content of sludge, which suggest that there is no significant effect on man or the food chain due to sludge-borne organics applied to land.

SLUDGE APPLICATION TO LAND IN RELATION TO OTHER DISTRICT SLUDGE MANAGEMENT OPTIONS

Current District Sludge Management Options

Because of the uncertainty surrounding federal and state regulatory policies on sludge processing, disposal, and utilization, the District currently employs the following sludge management options: (1) Sludge application to land (Fulton County and the Hanover Park Water Reclamation Plant); (2) Landfilling at privately owned sites (under contract to District); (3) Final closure of a city of Chicago landfill site; (4) Distribution to large scale users (sod farms, nurseries, golf courses, etc.); and (5) Landscaping purposes at District facilities (planting trees, grasses, use as top soil, etc.).

Prior to initiation of the Fulton County project (1972), the chief outlet for sludge produced in the District was the sale of heat-dried fertilizer; but from 1972 to 1981, this sludge management option was gradually reduced because of high energy costs until it was completely phased out in 1982.

Summaries of the existing District sludge management options are in the sections that follow.

City of Chicago Landfill Closure

In 1979, the District and the City of Chicago discussed the possibility of a joint cooperative program to reclaim a landfill owned by the City of Chicago. The landfill was 91 hectares (225 acres) in size and was used for the disposal of municipal solid waste, construction debris, curb and gutter cleanings, and tree removal wastes. The site was licensed and operated before the enactment of the current stricter environmental regulations, and it did not have a final cover, lacked runoff control, and had no vegetative cover.

In 1979, the City of Chicago and the District agreed to conduct a demonstration to show how District sludge might be used to convert the site at 103rd and Doty Avenue into an environmentally acceptable landfill which would be aesthetically pleasing to the surrounding neighborhood. The demonstration site was 14.9 ha (37 acres) in size. The site was covered with a 0.6 m (2 ft) clay seal, and then 1.52 m (5 ft) of sludge (60% solids or greater) was applied. The sludge that was applied was a combination of anaerobically digested sludge and air dried Imhof tank sludge. The whole area was then seeded with a rye grass mixture to establish erosion control. The project was a complete success and a vigorous stand of grass was produced.

The success of the demonstration project led to an inter-governmental cooperative effort between the District and the City of Chicago. In 1982, the City Council of Chicago passed an ordinance that established the District as the city agent in the final closure of the 103rd and Doty Avenue site.

The closure plan will be performed in three phases. Phase I will involve the development of a 23.4 ha (58 acre) winter recreation hill and parking area. The site will first be capped with a 0.6 m (2 ft) clay seal, and then a hill will be constructed from clean clay soil fill and air dried District sludge. The entire site will be bermed and runoff directed to drainage control ponds. The entire site will be landscaped with grass and trees.

Phase II will take place concurrently with Phase I. An 8.8 ha (22 acres) site which represents the most highly visible portion of the entire site will be capped with a 0.6 m (2 ft) clay seal and then 1.52 m (5 ft) of District sludge. Again, the entire site will be landscaped with grass and trees and runoff directed to ponds.

Phase III will involve the reclamation of the remaining 58.6 ha (145 acres) of the 103rd and Doty site. The site will receive 1.5 m (5 ft) of sludge followed by a 0.6 m (2 ft) clay cap and 0.6 m (2 ft) of sludge as a base for vegetative cover. The District will contour the site as dictated by the City of Chicago which has indicated that the site will be used for a golf course, public park, or tree nursery.

Distribution to Large Users: Landscaping at District Facilities

The District distributes a portion of its sludge (dried to at least 60% solids) to large-scale users such as golf courses, nurseries, and sod farms for landscaping purposes. Normally, the sludge is delivered free of charge to the user once a site inspection is made by District personnel. Most of the sludge is distributed to users within a 50-mile radius of the District facility where the sludge is produced.

Landfilling by Private Contractors

Periodically the District will utilize the services of various private landfills in the greater Chicago area when conditions so dictate. This method of sludge management has been used when the quantity of sludge to be distributed exceeds the capacity of the other options available. For example, it was necessary recently to dispose of a large quantity of sludge in a short period of time when a sludge lagoon had to be eliminated to make space for a plant expansion.

Quantities of Sludge Distributed Through Sludge Management Options

The five current sludge disposal options discussed above give the District a variety of outlets for its sludge production. The District believes that several viable sludge management options are necessary in order to insure that there is always an outlet for daily sludge production.

Table 25 presents the dry tonnage and percentage of sludge distributed via various District sludge management options used in 1983. The majority (50.48%) of District sludge was used for the final closure of the City of Chicago landfill site. The landfilling of sludge accounted for approximately 23% of the sludge distributed through the various options used in 1983. Sludge used for landscaping at District facilities and by large users amounted to about 17% of the sludge distributed in 1983.

TABLE 25. Disposition of sludge during 1983 at the Metropolitan Sanitary District of Greater Chicago.*

Disposition	Dry Tons	Percent of Total
Land Application - Fulton County	41,272	9.56
Land Application - Hanover Park	677	0.15
Landfilling - Private Contractor	99,778	23.11
Final Closure of City of Chicago Landfill	218,002	50.48
Distribution to Large Scale Users	31,402	7.27
Landscaping of District Facilities	40,715	9.43
TOTAL	431,846	100.00

*1983 Annual Report of the Maintenance and Operations Department of the Metropolitan Sanitary District of Greater Chicago.

Costs of District Sludge Management Options

Table 26 presents a summary of the costs of current District sludge management options. As can be seen, the District's Sludge Application to Land program at Fulton County is by far the most expensive sludge management option. This is mainly due to the high transportation costs. Because of these high transportation costs, the District discontinued barge transportation in August of 1983. The hauling of liquid digested sludge was simply too expensive to warrant its continuance.

The District is currently distributing most of its sludge (Table 25) to the City of Chicago landfill, and to private landfillers, and uses the rest for landscaping purposes (private users or at District facilities). This is because these methods (Table 26) are most economical at the present time.

The Fulton County site continues to operate using sludge on hand in the onsite lagoons. In 1984, a small quantity of dried sludge (greater than 60% solids) was shipped from the West-Southwest Sewage Treatment Works to the site by rail-car to determine whether this transportation scheme coupled with high solids content sludge might make this option more economically attractive.

TABLE 26. 1983 sludge management costs (dollars per dry ton).

Item	Application of Liquid Sludge at Fulton County	City of Chicago Landfill Closure Using Air-Dried Sludge	Landfilling of Lagoon Sludge	Distribution of Air-Dried Sludge to Large Users and Landscaping of District Facilities
Capital Costs	25.72	-	-	-
Land Cost and Taxes	9.77*	-	-	-
Application Costs	86.04*	-	-	-
Gravity Concentration	4.55	4.55	4.55	4.55
Concentration (vacuum filter)	24.93	24.93	24.93	24.93
Digestion	14.15	14.15	14.15	14.15
Centrifugation	-	53.84	-	53.84
Agitation Drying	-	18.04	-	18.04
Concentration in Lagoons & Transportation	-	-	59.92	-
Transportation Only	-	15.83*	-	-
Loading & Transportation	141.78	-	-	-
Landfill (private contractor)	-	-	8.66*	-
Sale of Crop	-3.09	-	-	-
TOTAL	303.85	131.34	112.21	124.30

*1981 costs.

CONCLUSIONS

This paper has attempted to discuss the occurrence of metals and organics in municipal sewage systems and municipal sludge and provide information about the fate of these constituents in the soil, plants, and animals at municipal sludge application to land sites. Based upon studies reported in the literature, and information compiled by the District, principally at its Fulton County land application site, the following general conclusions were reached:

1. Municipal raw sewage contains most of the metals and many organics, depending upon the nature of the drainage basin served.
2. Municipal sewage treatment facilities remove a substantial amount of the metals and organics from raw sewage. Many of these constituents become associated with the sludge resulting from such treatment. Generally, sludge constituent concentrations are related to the presence of these constituents in the raw sewage.
3. As would be expected, sludge application raises the metal content of surface soil in proportion to the sludge application rate.
4. Although sludge application can raise the concentration of certain metals in crops, such uptakes can be managed by controlling application rates. If application rate control is impractical, crops can be marketed for nonfood chain uses or for animal feed.
5. Sludge applied metals will not affect groundwater and surface water at well managed sludge application to land sites.
6. Studies show that if metal translocation to animals from sludge application to land occurs at all, it will occur in the animal organs and not in the muscle tissue. Since most meat consumed by humans is muscle tissue, and most is produced from land which receives no sludge application, there is no danger to the human diet from translocation of sludge metals to animals.
7. The data presented in this report show that the soil has a high affinity for the organics contained in municipal sludge. Therefore, like the metals, the organics in the sludge pose no hazard to surface and groundwater at well managed sludge application to land sites.
8. It is reasonable to conclude that translocation and uptake of organics into plant tissue play a very minor role (if any) in determining the fate of organics in sludge applied to land.
9. The data on the public health effects of organics in sludge applied to land is meager. However, there have been some studies, principally related to the PCB content of sludge, which suggest that there is no significant effect upon man or the food chain due to sludge-borne organics applied to land.
10. Sludge application to land is only one option available for managing municipal sludge. Use of this option must always be weighed against the cost and environmental impact in relation to other options.

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LOADING RATES AND FREQUENCIES FOR LAND TREATMENT SYSTEMS

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INTRODUCTION

Hazardous Waste Land Treatment (HWLT) can be considered as the intimate mixing or dispersion of wastes into the upper zone of the soil-plant system with the objective of microbial stabilization, detoxication, and/or immobilization leading to an environmentally acceptable assimilation of the waste.

HWLT also is based on the constraint of nondegradation of land. That is, the waste when considered on a constituent-by-constituent basis is applied to the plant-soil system at such loading rates and frequencies, and over such limited time spans, that no land is irreversibly removed from some other potential societal usage such as agriculture, development, and forestation.

Soil-site assimilative capacity (SSAC) and nondegradation of the environment are directly related to the loading rate and the frequency of waste application. The overall goal is the simultaneous ultimate disposal and treatment of hazardous wastes, while ensuring protection of the public health and the environment. Figure 1 contains the elements related to this goal.

A simple model of a hazardous waste land treatment system is shown in Figure 2. The soil-waste treatment zone receives a waste with a flow and frequency pattern (Q) and hazard values (H) for each individual constituent of concern (i). The waste is generally incorporated into the treatment zone through mixing. For example, a principal hazardous constituent (PHC) of an applied waste, PHCi, is treated in the soil-waste treatment zone. Treatment occurs through the processes of degradation, transformation, and immobilization. Monitoring the soil-core and soil-pore liquid below the treatment zone provides information concerning the effectiveness of treatment, which is compared to criteria for treatment requirements. Management options for the system to achieve treatment requirements can then be based on feedback control. The system can be managed to optimize treatment through site/soil modification or through adjustment of loading variables, including loading rate and loading frequency.

Recently promulgated HWLT regulations (40 CFR section 264) requires that a permit be obtained to operate a HWLT facility. Requirements of the regulations

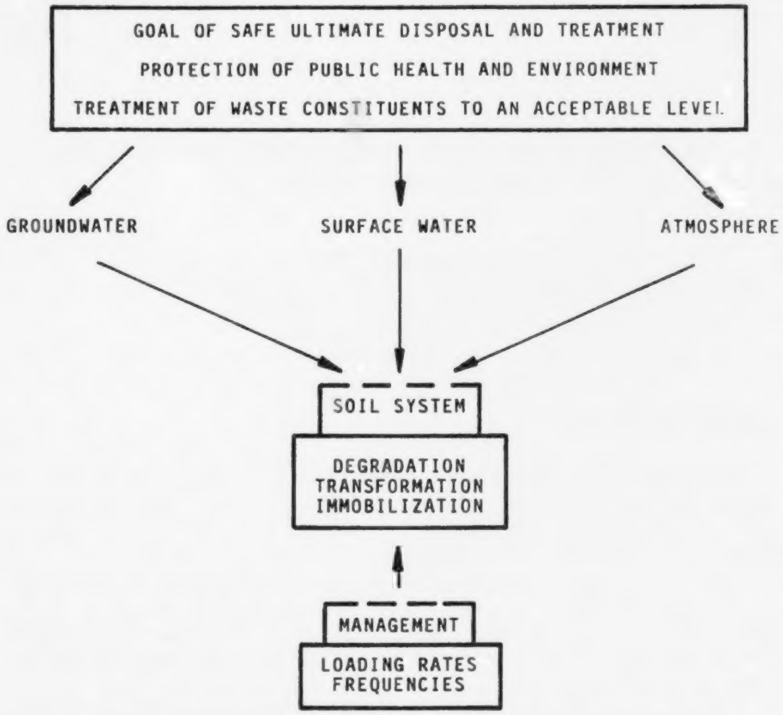
GOAL OF SAFE ULTIMATE DISPOSAL AND TREATMENT
PROTECTION OF PUBLIC HEALTH AND ENVIRONMENT
TREATMENT OF WASTE CONSTITUENTS TO AN ACCEPTABLE LEVEL
GROUNDWATER
SURFACE WATER
ATMOSPHERE
SOIL SYSTEM
DEGRADATION
TRANSFORMATION
IMMOBILIZATION
MANAGEMENT
LOADING RATES
FREQUENCIES

FIGURE 1. Elements related to the goal of hazardous waste land treatment.

specify that to obtain a permit it must be demonstrated that any hazardous constituents contained in the waste to be land applied must be degraded, transformed, and/or immobilized in the soil treatment zone. The regulations also require that a treatment demonstration study be conducted in order to establish what combination of operating practices can be used such as: (1) waste application rate, (2) waste application frequency, (3) waste application method, (4) measures to control soil pH, (5) measures to increase microbial activity, (6) measures to increase chemical reaction, and (7) measures to control soil moisture.

INTERFACING RCRA AND CERCLA FOR LAND TREATMENT

Considering the relatively undeveloped state-of-the-art of remedial clean-up under the Comprehensive Environmental Response Compensation, and Liability Act of 1980 (CERCLA), a logical approach to in situ treatment of hazardous waste at uncontrolled sites is to utilize the concepts and information developed for land treatment of hazardous waste under the Resource Conservation and Recovery Act of 1976 (RCRA). RCRA regulations combined with information available concerning land treatment principles and practices for nonhazardous municipal and industrial waste (Overcash and Pal 1979; Elliott and Stevenson 1977; Loehr 1976; Sanks and Asano 1976; Torrey 1979), and for hazardous wastes (U.S. EPA 1983; Dupont et al. 1985; Sims 1984; Sims et al. 1985) provide a basis for developing an approach to in situ treatment of hazardous wastes at sites addressed by CERCLA.

PROCESSES AFFECTING LAND TREATMENT OF HAZARDOUS WASTES

Microbial degradation and soil adsorption are the principal processes which should be considered in hazardous waste land treatment. It must be determined whether the residence time in the treatment zone will be sufficient to allow microbial degradation and detoxication of organic constituents. Biological degradation and transformation are the principal mechanisms responsible for the destruction and detoxication of organic waste constituents in soil systems.

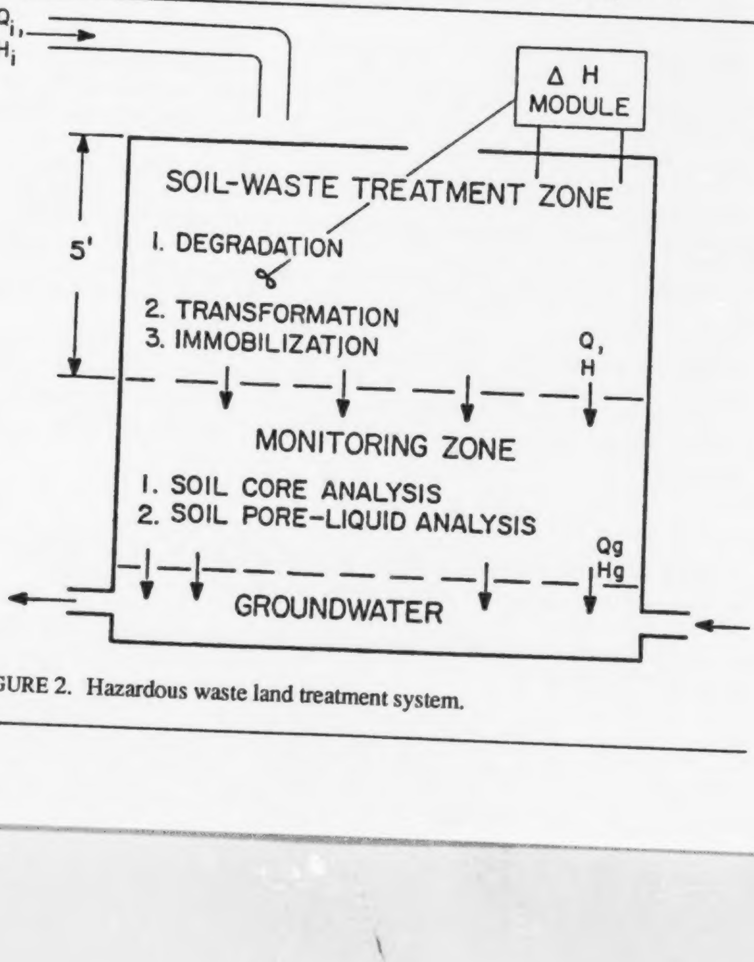
Qi, Hi
Δ H MODULE
SOIL-WASTE TREATMENT ZONE
5'
1. DEGRADATION
2. TRANSFORMATION
3. IMMOBILIZATION
Q, H
MONITORING ZONE
1. SOIL CORE ANALYSIS
2. SOIL PORE-LIQUID ANALYSIS
Qg Hg
GROUNDWATER

FIGURE 2. Hazardous waste land treatment system.

Individual biochemical pathways involved in contaminant degradation, detoxication, and mineralization may require separate mathematical representations. Equation 1 is the expression most widely used in modeling the degradation of organic compounds in soil systems because of its inherent simplicity and effectiveness in describing observed results.

$$dC/dt = -KsC \tag{1}$$

where C = contaminant concentration, mass/mass, t = time, and Ks = first order rate constant, l/time.

A parameter associated with the first order rate model, the "half-life" of an organic compound, is commonly used to describe the biological disappearance of a parent compound in soil systems. The half-life of a constituent is assumed independent of the initial concentration in the soil system and is mathematically expressed as:

$$t\ 1/2 = 0.693/Ks \tag{2}$$

where t 1/2 = half-life of the constituent in the soil system, time.

It is important to realize that biodegradation and biotransformation reactions and kinetics are influenced by waste, site, soil, and climate characteristics. These factors, as they directly affect waste assimilative capacity of the soil through affecting the rate of mineralization, are also important in determining waste loading rates and waste application frequencies.

Soil sorption is the physical/chemical process which involves an increase of solute concentration at the soil-water interface. Soil sorption is perhaps the most important process affecting immobilization of organic constituents present in hazardous wastes. Leaching potential and the residence time in soil for organic constituents, which undergo biodegradation, are directly affected by the extent of immobilization. Therefore, it is important to examine soil sorption of organic compounds in order to optimize treatment by immobilization.

The sorption process is usually described by an adsorption isotherm, which expresses the relationship between the amount of constituent adsorbed to a solid (soil), and the concentration of solute in solution at equilibrium. One frequently used and useful adsorption isotherm is the Freundlich isotherm which is expressed as:

$$S = (K)C^N \tag{3}$$

where S = amount of organic compound adsorbed per unit soil dry weight,
K, N = constants, and C = solution phase equilibrium concentration.

The constant K represents the extent of sorption, i.e., the higher the K value, the greater the sorption.

The Freundlich isotherm provides a great deal of flexibility in that the use of the two equation parameters, K and N, allows the fitting of the equation to a wide range of data, and it does not require a maximum limit for the amount of substance adsorbed. Because of the general applicability of this isotherm, it is used extensively and has been proposed for use with a transport equation to describe the movement of organic chemical pesticides in soil systems (Van Genuchten et al. 1974).

The linear isotherm is an important application of the Freundlich isotherm and is generated from Equation 2 when N = 1. The linear isotherm may be expressed as:

$$S = (Kd)C \tag{4}$$

where Kd = distribution coefficient.

If the rate of transport (leaching) is significant compared with the rate of biodegradation, both factors must be considered (degradation and leaching). The constitutents may reach a "critical depth" in the soil, which may be the end of the microbially active zone, groundwater, or end of the soil zone, before being degraded or detoxified. Mathematical models and/or experimental studies with the soil waste mixtures may be used to assess migration and degradation patterns (Sims et al. 1985).

EXPERIMENTAL STUDIES TO DETERMINE LOADING RATES AND FREQUENCIES

Short-term experimental studies (approximately 20 weeks) can be used to establish the feasibility of land treatment, appropriate initial waste loading rates, and preliminary information concerning frequency of waste application for a site-specific and waste-specific condition. Treatability studies can also be used to optimize management and effectiveness of treatment when land treatment is feasible. Short-term testing can establish the following specific information with respect to a specific site/waste/soil condition: (1) The critical initial soil concentration or loading rate for a waste at which degradation and detoxication become ineffective; (2) The rate of biodegradation of organic constituents; (3) Deactivation of mutagenic characteristics and cellular detoxication to determine when the waste is no longer toxic; and (4) Criteria for management of the soil and site to enhance the natural ability of the soil to assimilate constituents by determining optimum conditions for degradation, detoxication, and immobilization.

A protocol for obtaining design and management information with respect to loading rates and application frequencies, based on the specific criteria identified above, has been developed and is being utilized for a variety of hazardous wastes at the Utah Water Research Laboratory. The three-step protocol includes: (1) soil incubation, (2) chemical characterization, identification, and quantification, and (3) determination of cellular and genotoxicity reduction. The protocol interfaces chemical information and bioassay information concerning treatment effectiveness. Engineering management options for soil incubation to optimize treatment can also be selected. The protocol provides a rapid and quantitative tool for obtaining critical information concerning loading rates and application frequencies, and engineering management options for influencing loading rates and application frequencies in order to optimize safe ultimate treatment.

Determination of an initial waste loading rate requires information for each of the five criteria identified above. HWLT regulations restrict land treatment to wastes which can be rendered less or nonhazardous in the soil. Cellular toxicity is one characteristic for which a waste is considered to be hazardous. If a waste or waste constituent exerts toxic effects on human health or the environment, toxicity reduction as a function of incubation time in the soil can be used to assess the success of treatment and provide information concerning a loading rate.

The toxicity test procedure selected for inclusion in the protocol was developed and evaluated by the HWLT research group at the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma, for this purpose (Matthews 1983, Matthews and Bullich 1984, Matthews and Hastings 1985). The procedure utilizes toxicity reduction of acutely toxic organics contained in the water soluble fraction (WSF) of extracted waste-soil mixtures as the measurement criterion. Acute toxicity is measured using the Microtox test system.

The Microtox System utilizes a suspension of luminescent bacteria (Photobacterium phosphoreum) as bioassay organisms for measuring acute toxicity in aqueous samples. The assay system is an instrumental approach in which bioassay organisms are handled like a chemical reagent. Suspensions with approximately 1,000,000 bioluminescent organisms are "challenged" by the addition of the chemicals in an unknown sample.

The Microtox test is conducted by first preparing a water extract of the waste: soil sample and then subjecting the Microtox System test organism to various dilutions of the extract. The dilution resulting in a 50% reduction in light output by the test organism is termed the EC50 (EC = effective concentration) for the waste:soil mixture.

Numerous evaluations of acute toxicity measurements utilizing this system have revealed that Microtox is sensitive to a wide spectrum of toxicants with results correlating favorably with other bioassay procedures (Qureshi et al. 1982, Casseri et al. 1983, Burks et al. 1982). A comprehensive discussion of the Microtox System, including its special merits and limitations, principles of operation, operating procedure, and basic data reduction schemes, has been prepared for distribution by Beckman Instruments, Inc. (1982).

Use of the Microtox System for screening purposes is based on the assumption that land treatment (assimilation) potential for a soil:waste mixture is primarily a function of waste loading rate and waste application frequency. Water soluble fraction (WSF) toxicity of a soil:waste mixture, as indicated by the Microtox System, is used as the criterion for determination of adverse soil loading impacts.

For loading rate determination the Microtox System may provide a loading rate that considers the first and third criteria (initial loading rate and detoxification). When using uncontaminated or unacclimated soil as the receiving medium for the waste, a positive land treatment potential is indicated when the following results are obtained in the Microtox System: (a) The initial (day 0) extract of the soil:waste mixture may demonstrate an EC50 (effective concentration of extract resulting in a light reduction of 50%) value of between 20 and 60% of extract, i.e. an 80 to 40% dilution with distilled water; and (b) the extract of the soil: waste mixture is nontoxic to test organisms after 42 days of soil incubation and treatment. Results obtained by Matthews and co-workers (1983, 1984, 1985) at the RSKERL indicate that WSF acute toxicity of most complex wastes defined by the Microtox System using unacclimated soil will not be significantly reduced if the initial soil:waste extract EC50 is less than 20% (a minimum 80% dilution).

High performance liquid chromatography (HPLC) analysis of soil-waste extracts can be used to obtain information with regard to criteria (2) and (4). HPLC analysis can be used to identify and quantify parent compounds and to determine the rate(s) of degradation in soil surface layers and subsurface layers. Leachates generated in soil systems may also be characterized for parent constituents. HPLC chromatograms may also be used to characterize the rate and extent of formation of degradation products and the rate of degradation of metabolites. Information obtained for criterion (2), rate of degradation, will affect the frequency of application of waste. Information obtained for criterion (4), engineering management options, will affect both rate and frequency of application.

The Ames *Salmonella typhimurium* assay is used to obtain information with regard to criteria (3), mutagenicity, and (4), engineering management options. The Ames assay can also be used to determine the mutagenic potential of partially degraded constituents in soil systems. The Ames assay utilizes the bacterium *Salmonella typhimurium* to indicate the presence of mutagenic constituents. Strains of *Salmonella typhimurium* bacteria can be selected to indicate the mechanism of mutagenicity, i.e. point mutations or frame-shift mutations. Mutagenicity is scored as a ratio of the number of bacterial colonies in the presence of a test sample to the number of colonies in the absence of the test sample. Since growth occurs in proportion to mutagenic potential, growth will be greater in the presence of a mutagen. The minimum mutagenic ratio, i.e. ratio of number of colonies in the presence of a test sample to the number of colonies on a control growth plate in the absence of the test sample, is 2.0. Therefore, a sample exhibiting a mutagenic ratio greater than 2.0 is considered to possess mutagenic properties.

The Ames assay may be used to assess the mutagenic potential of the water soluble fraction (soil-pore liquid) and the water insoluble fraction (soil core). The information obtained may be used for determining the appropriateness of both the loading rate, selected on the basis of the Microtox Data, and the application frequency, selected on the basis of chemical analyses for determination of the rate of biodegradation, for the waste-soil mixture.

With the initial loading rate selected based on the Microtox Data and the initial frequency of waste application based on the rate of biodegradation of parent constituents, information may be obtained regarding acclimation of the soil:waste mixture.

RESULTS OF EXPERIMENTAL STUDIES TO DETERMINE LOADING RATES AND FREQUENCIES

Utilizing the protocol described previously to obtain information for the specific criteria of a treatability study, loading rate and application frequency information has been generated for several hazardous wastes. Results presented here serve to illustrate the use of the protocol described for the determination of the required information.

Initial Loading Rate

Results of the Microtox test, used for determining the initial soil loading rate of a waste, are presented in Table 1 for several wastes. The EC50 values presented represent a dose-response curve and indicate the effect of increasing waste load on microorganism toxicity. An initial (day 0 extract) EC50 value of approximately 20% is used to indicate the waste loading rate above which toxicity reduction is not significant, and treatment is ineffective. Results of the Microtox

TABLE 1. Microtox test results for wastes containing PAH compounds.

Waste:Soil (Ratio)	Complex Waste Day 0 EC 50 (5,15°) Value (percent)+ Waste 1	Waste 2	Waste 3
1:99	18*		
2:98	14		
4:96	10	60	
5:95			21*
7:93			11
8:92		28	
12:88			6
16:84		33	6
33:67			5
67:33			2
100:0		12	2
0:100	>100**	>100**	>100**

+EC50 (5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

*Denotes the critical soil level (loading rate) based on day 0 results.

**An EC50 value greater than 100 indicates that the sample is not toxic to the microorganisms; the actual value is not significant.

test indicate that waste loading rates (using the EC50 value of 20%) vary and are a function of waste characteristics. For wastes 1, 2, and 3, critical soil loading rates are 1:99, 20:80, and 5:95 for waste:soil ratios (by weight), respectively. These results illustrate the effect of waste type on initial loading rate using the same soil for all three wastes.

Table 2 illustrates the rate of detoxication for pentachlorophenol waste incubated in Durant clay loam at three different initial loading rates. The information presented indicates that at the highest loading rate, i.e., 0.8 percent, the waste was not detoxified to a nontoxic level by day 42. Based on these results for initial (day 0) toxicity and for the rate of detoxication, loading rates were selected for long-term degradation and immobilization (column) studies. Three soil loading rates selected for further study, based on results of the Microtox System, for pentachlorophenol were 0.3, 0.5, and 0.7% for the Durant clay loam.

The effects of waste type and soil type on initial loading rate for unacclimated soil, based on results of Microtox System testing, including initial toxicity and the rate of detoxication over a 42-day incubation period are presented in Table 3. Results indicate that petroleum wastes could be applied at loading rates much higher than for wood preserving wastes. Also, for all wastes investigated higher loading rates were possible with the Durant clay loam compared with the Kidman sandy loam.

FREQUENCY OF WASTE APPLICATION DETERMINED BY RATE OF TREATMENT

The frequency with which a hazardous waste may be reapplied to a site/soil system is dependent upon the extent and rate of treatment, including detoxication and degradation. The extent of treatment required can be chosen as a percent increase over background level or as a percent reduction in the initial waste concentration in the soil. The extent of detoxication required with the Microtox System before reapplication of the waste is indicated by a change in EC50 values from 20% (initial application) to approximately 60%. The extent of detoxication for mutagenic constituents can be evaluated with the Ames assay. A reduction in mutagenicity for the incubated soil/waste extract to 100% reduction (no mutagenic potential) or some fraction of this value may be chosen. The extent of degradation of principal hazardous constituents (PHCs) identified in the waste may also be chosen as the parameter for monitoring to determine the extent of treatment before reapplication of waste. The most conservative parameter (detoxication or degradation) should be chosen for determining successful treatment before waste reapplication to the site/soil.

The rate of detoxication may also be determined with the Microtox System and with the Ames assay. Using the Microtox System, the rate of detoxication may be determined as time required for the soil:waste mixture to demonstrate an EC50 value of 60%. For the pentachlorophenol waste indicated in Table 2, based on the Microtox System results, waste reapplication could occur between day 0 and day 14 for the 0.2% loading rate and day 14 for the 0.4% loading rate. At the highest loading rate, 0.8%, the waste reapplication time could not be determined, since the EC50 value did not increase to a value of approximately 60% over the 42 day incubation period.

TABLE 2. Microtox results for pentachloropheonol:Durant clay loam mixtures (42-day incubation).

Loading rates*	EC50 (5,15°)+ Values (Percent)			
	Day 0	Day 14	Day 28	Day 42
0.2%	44.6	NT**	NT	NT
0.4%	32.8	66.8	96.8	NT
0.8%	16.9	24.7	30.8	22.6

+EC50 (5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample additon at a temperature of 15°C.

*Loading rates expressed as % waste wet weight/soil dry weight.

**NT=nontoxic. This means that the EC50 value is greater or equal to 100%.

Results for detoxication and degradation for a complex fossil fuel waste containing polynuclear aromatic (PNA) constituents treated in unacclimated soil are shown in Tables 4 and 5, and in Figures 3 and 4. Microtox System values are shown in Table 4. Degradation kinetics including first order rate constants, half-lives, and percent reductions for PNA constituents for the waste are given in Table 5. Mutagenic potentials for extracts of the soil:waste mixture as a function of incubation time are indicated in Figures 3 and 4. Results indicate that the mutagenic characteristics deactivation to a borderline mutagenic level has occurred after 42 days of incubation of the soil:waste mixture.

Based on the results presented for chemical analysis by HPLC for determination of parent compound degradation, Microtox System results for the water solute fraction (soil-pore liquid), and Ames assay results for mutagenic constituents in the soil core, decisions can be made concerning the frequency of reapplication. Incubation for a period of 90 days was required for unacclimated soil to achieve reductions of approximately 50% for parent compounds and to achieve water-soluble fraction toxicity reduction. Mutagenic characteristics deactivation required approximately 42 days. Therefore, an initial frequency of waste application may be chosen as 90 days.

Although initial loading rates and application frequencies have been determined for the waste described above, acclimation of soil microorganisms to the applied waste may allow increased loading rates and application frequencies. This may occur through repeated applications of the waste to the soil, and/or use of engineering management options to optimize degradation and detoxication of waste constituents in the soil.

TABLE 3. Soil loading rates for wastes based on microtox results.

Waste	Loading Rates Kidman Sandy Loam Low	 Medium	 High	 Durant Clay Loam Low	 Medium	 High
	(% waste wet weight/soil dry weight)					
Creosote	0.4	0.7	1.0	0.7	1.0	1.3
Pentachlorophenol	0.075	0.15	0.3	0.3	0.5	0.7
API Separator Sludge	6	9	12	6	9	12
Slop Oil	6	8	12	8	12	14

EFFECT OF ACCLIMATION ON RATE AND EXTENT OF TREATMENT

The process of acclimation of the soil to an applied waste would be expected to have a significant influence on the ability of the soil to treat the waste through biodegradation and detoxication. Experimental and field studies have indicated the importance of soil acclimation. Khesina et al. (1969) investigated the degradation of B(a)P in soils under natural conditions of temperature and soil moisture. A control soil (C) with no history of pollution, a moderately polluted soil (M), and a highly oil-contaminated soil (N) were studied. Also, a control soil with B(a)P added to increase the level to that of the (N) soil was incubated (B). The results are presented in Table 6.

TABLE 4. Detoxication of fossil fuel waste in soil indicated by Microtox System.

Time (days)	EC50 (5,15°) Value
0	21
42	19
91	40

TABLE 5. Rate of degradation of polynuclear aromatic hydrocarbons in fossil fuel waste for 90 days, 2 incubations.

PNA	Co: Concentration in Soil/Waste at Time 0 (ppm)	First Order Degradation Rate Constant (day-1)	Half-Life in Soil System (days)	Decrease from Time 0 (%)
Acenaphthylene	392	0.0089	78	55
Acenaphthene	818	0.0072	96	48
Fluorene	56	0.0108	64	62
Phenanthrene	30	0.0101	69	61
Anthracene	38	0.0247	28	89
Fluoranthene	154	0.0067	104	45
Pyrene	177	0.0094	73	58
Benz(a)anthracene	30	0.0056	123	42
Chrysene	27	0.0099	70	59
Benzo(b)fluoranthene	21	0.0082	85	51
Benzo(k)fluoranthene	14	0.0049	143	38
Benzo(a)pyrene	10	0.0076	91	50
Benzo(ghi)perylene	146	0.0094	74	57
Dibenz(a,h)anthracene	27	0.0039	179	27
Indeno(1,2,3-cd)pyrene	9	0.0121	57	68

Acclimation refers to the process whereby the site/soil has been exposed to the presence of PNA constituents over a time period before introduction of additional PNA constituents. Results clearly show that degradation of B(a)P can be obtained under natural conditions and with natural soil microbial populations. Also, the rate of transformation appears to be a function of the soil concentration for soils that are acclimated to the presence of PNAs. Soils (M) and (N) achieved similar percent reductions in B(a)P over 3 months although initial soil levels of B(a)P differed by a factor of 50. For nonacclimated soils reductions in B(a)P were very low, some soils showing no reduction in B(a)P. Thus, B(a)P has been demonstrated to be degraded in soil systems, with the extent and rate of degradation influenced by the history of the site/soil, i.e. acclimated or nonacclimated.

The extent of acclimation of creosote waste applied to Durant clay loam at 1% loading rate (waste wet weight/soil dry weight) at two-week intervals was observed in experiments at the Utah Water Research Laboratory. Using unacclimated soil, the rate of reduction in PNA constituents was not observed to increase or significantly decrease over the relatively short duration (6 weeks) of the experiments. Thus, it was not possible to quickly acclimate the clay loam soil to creosote waste with frequent reapplications of the waste.

Acclimation of the soil to the complex fossil fuel waste described in Tables 4 and 5, and Figures 3 and 4 is demonstrated by the results presented in Table 7.

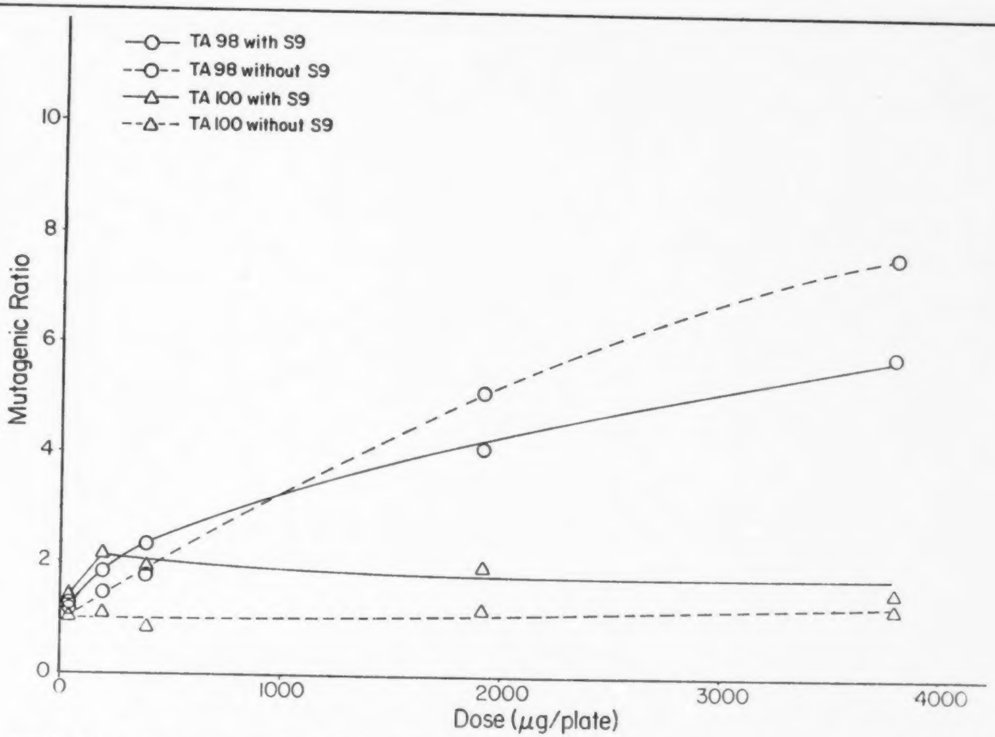

FIGURE 3. Ames assay results for waste; soil mixture immediately after waste incorporation into soil.

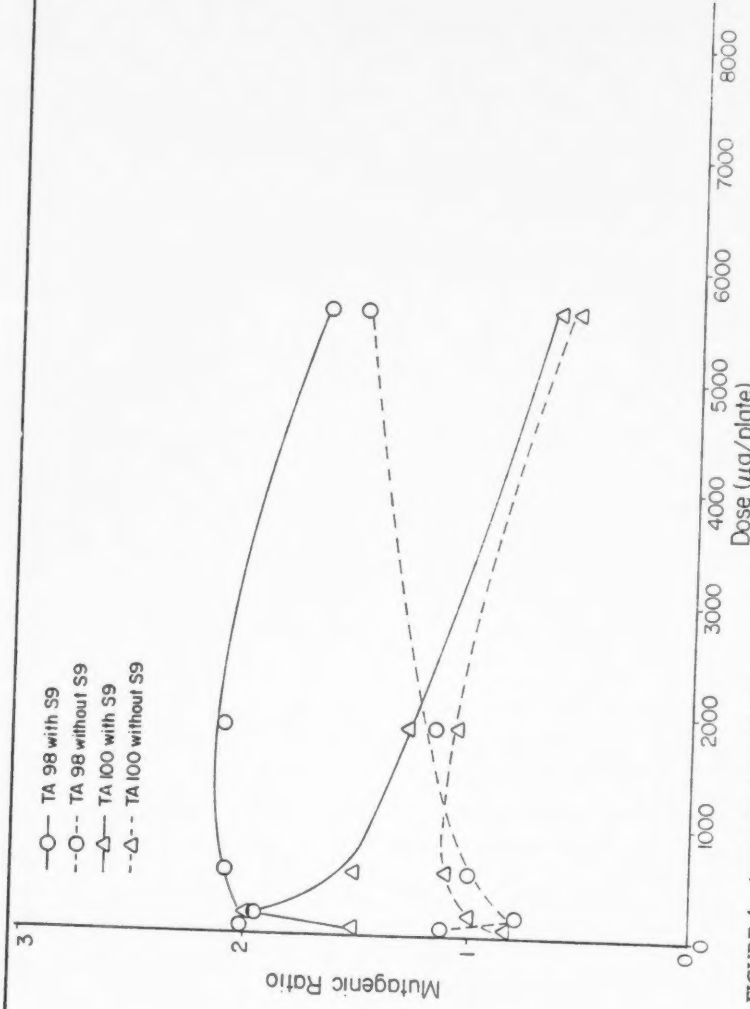

FIGURE 4. Ames assay results for waste; soil mixture after forty-two days incubation.

TABLE 6. Degradation of benzo(a)pyrene by soil microorganisms (Khesina et al. 1969).

Soil	Co[a]	B(a)P content of soil 1 mon exposure (mg/kg soil)	2 mon exposure (mg/kg soil)	3 mon exposure (mg/kg soil)	Reduction at 3 mon (%)
C[b]	9.5	7.4	7.5	6.3	33
M[c]	545	377	346	159	71
B[d]	29,200	29,300	29,000	30,100	0
N[e]	28,500	16,000	16,700	13,700	52

[a]Co = initial soil concentration (μg/g soil).
[b]C = control soil with no history of pollution.
[c]M = moderately oil-polluted soil.
[d]B = control soil with B(a)P added to increase the level to that of the (N) soil.
[e]N = highly oil-contaminated soil.

The table shows the reduction of PNA constituents for the initial loading rate of waste in unacclimated soil compared with the reduction of constituents after the second application event (after 168 days of waste:soil incubation). From results presented in Table 7, it is clear that greater degradation of PAH constituents was achieved in less time during the second waste application event.

ENGINEERING MANAGEMENT TECHNIQUES FOR OPTIMIZING LOADING RATES AND FREQUENCIES

Engineering management techniques represent amendments which the hazardous waste engineer may use to increase the assimilative capacity of the soil for an applied waste. Amendments which increase the site/soil assimilative capacity for a waste directly affect the loading rate and application frequency for land treatment.

The effects of amendments on the degradation kinetics of B(a)P applied as a pure compound to soil batch reactors is presented in Table 8 (Sims and Overcash 1984). Results suggest that it may be possible to influence the degradation rate of PNA constituents, especially with pH amendment and analog enrichment tech-

TABLE 7. Acclimation of soil to complex fossil fuel waste.

PNA Constituent	Unacclimated Soil: Initial Soil Concentration (mg/kg-dry wt)	Unacclimated Soil: Reduction in 40 days (%)	Acclimated Soil: Soil Concentration after First Reapplication of Waste (after 168 days incubation at initial level) (mg/kg-dry wt)	Acclimated Soil: Reduction in 22 days (%)
Naphthalene	38	90	38	100
Phenanthrene	30	70	30	83
Anthracene	38	58	38	99
Fluoranthene	154	51	159	82
Pyrene	177	47	180	86
Benz(a)anthracene	30	42	40	70
Chrysene	27	25	33	61
Benz(a)pyrene	10	40	12	50

TABLE 8. Effect of amendments on benz(a)pyrene degradation.

Treatment	Half-Life (Days)
None	90A[a]
Nutrients	81A
pH adjustment from 5.2 to 7.4	64B
Surfactant	87A
Analog enrichment with phenanthrene	64B

[a] Values represent means of three replicates. Means followed by the same letter are not significantly different at the 0.05 level.

niques. The degradation of B(a)P, a five ring compound which is considered to be co-metabolized, i.e., cannot serve as a source of carbon and energy for the growth of microorganisms, appears to be influenced by the addition of a PNA compound that can serve as a source of carbon and energy (phenanthrene). Statistical analysis of the data indicated statistically significant differences among the treatments, as shown in Table 8.

The effects of moisture amendment on the degradation of pure PNA compounds applied to soil batch reactors is presented in Table 9 (Umfleet et al. 1984). The effect of soil moisture on PNA degradation was evaluated by operating a set of soil reactors at 20–40% and at 60–80% of field capacity. Results given in Table 9 indicate that optimum degradation occurred when soil moisture was maintained at 60–80% of field capacity.

The effects of addition of a complex amendment, manure, and pH adjustment on the degradation kinetics of PNA constituents present in the complex fossil fuel waste previously discussed are presented in Table 10. Manure addition was calculated based on nutrient content. However, manure also provided an inoculum of microorganisms and degradable organic carbon sources for soil microorganisms. pH of the waste:soil mixture was adjusted from 6.1 to 7.5. Results are presented for PNA constituents identified and quantified in waste:soil mixtures without and with the amendments described.

Results presented in Table 10 indicate that degradation of all PNA constituents was affected by the amendments. PNA half-lives were greatly reduced compared with half-lives in unamended soil. Thus, results for amendment additions to complex waste indicate that management techniques are available for optimizing degradation kinetics of parent constituents in soil systems.

TABLE 9. Effect of soil moisture on PNA degradation (results presented as half-life in days).

Moisture	Anthracene	Phenanthrene	Fluoranthene
20-40% field capacity	43	61	559
60-80% field capacity	37	54	231

SUMMARY

Determination and management of waste loading rates and application frequencies requires investigation and understanding of the chemical, biological, and physical behavior and fate of waste constituents in the soil/waste system. The protocol developed for determining initial loading rates and application frequencies presented provides a rapid method for interfacing chemical and bioassay information for determining land treatment potential for a hazardous waste. The protocol also provides a way to generate information concerning soil treatment optimization using engineering management techniques to increase the site/soil assimilative capacity which directly address degradation and detoxication. The information generated is therefore directly related to identification and selection of waste loading rates and application frequencies.

With regard to land application of hazardous waste under RCRA regulations or reclamation of hazardous waste contaminated soil as a result of unplanned or uncontrolled events, the same principles and techniques can be used to accomplish treatment and safe ultimate disposal. Processes controlling the behavior and fate of organic waste constituents in soil systems include biodegradation and sorption. These processes have been investigated and evaluated, and techniques have been developed to control these processes using the protocol and criteria discussed.

More research is required to characterize the mobility and toxicity and biodegradation of daughter products of principal hazardous constituents in soil systems. Results of treatment studies obtained thus far indicate that, with a better understanding of these processes, it will be possible to accomplish safe ultimate disposal and ensure the protection of public health at reasonable cost to society.

TABLE 10. Effect of manure and pH amendments on PNA degradation in a complex waste incorporated into soil.

PNA Compound	Half-Life in Waste:Soil Mixture (days) Without amendments	With amendments
Acenaphthylene	78	14
Acenaphthene	96	45
Fluorene	64	39
Phenanthrene	69	23
Anthracene	28	17
Fluoranthene	104	29
Pyrene	73	27
Benz(a)anthracene	123	52
Chrysene	70	42
Benzo(b)fluroanthene	85	65
Benzo(k)fluroanthene	143	74
Benzo(a)pyrene	91	69
Benzo(ghi)perylene	74	42
Dibenz(a,h)anthracene	179	70
Indeno(1,2,3-cd)pyrene	57	42

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MONITORING THE UNSATURATED ZONE

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ABSTRACT

Unsaturated zone monitoring systems are required at hazardous waste land treatment facilities to determine if pollutants are moving below the treatment zone. Either soil pore liquid samples or soil samples may be used to detect the presence of contaminants. There are a variety of liquid sampling devices in use, i.e., porous suction cups that are typically made of unglazed ceramic and pan samplers that depend on free drainage to provide a sample. While either of these methods may provide samples, porous cup samplers have the following disadvantages: (a) often they do not collect an adequate sample volume from clay soils, and (b) uncertainties about the spatial and temporal representativeness of the sample exist. In addition, special precautions are needed to prevent the loss of volatiles during sample collection. Pan samplers theoretically should not work in unsaturated soil but have been shown to work reasonably well in structured soils. They do not, however, work well in sandy soils. Their reliability under long-term field conditions has not been tested. Soil samples may be utilized to determine what is present in the soil at a given time and depth, but they are of little use for detecting highly mobile contaminants. Also, small soil samples may not adequately detect contaminants, since the movement of water and pollutants in structured soils occurs mainly in the large pores often found between structural units. While this could be partially overcome by collecting larger soil samples, the process is cumbersome. When a large enough sample is collected, the contaminants may be diluted to concentrations below detection levels.

More recent approaches that may alleviate some of these problems are discussed, i.e., using an undisturbed unit of soil enclosed in a container with walls, a bottom, and equipped with porous suction cups to collect leachate samples. Such devices may be buried in the ground below the land treatment facility and should provide representative samples of contaminants that leach through the soil. An alternative approach currently being developed is the use of a wick buried in the soil to continuously draw samples of soil solution for analyses. Both of these methods appear promising but require more development and testing.

INTRODUCTION

A variety of systems have been developed and utilized to monitor the movement of water and pollutants through the unsaturated zones found between the soil surface and the groundwater table. Much of the early work (Prince 1923; Reeve and Doering 1965) was done by researchers who were concerned about the mobility of nutrients, salts, and pesticides from agricultural activities. Unsaturated zone monitoring systems also have been used for research purposes to evaluate the mobility of chemicals that may be spilled on the soil surface or to monitor the mobility of a mixture of chemicals from land treatment facilities. Recent federal legislation (Federal Register 1985) now requires that unsaturated zone monitoring be utilized to provide an early warning of mobility under hazardous waste land treatment facilities.

To determine if a pollutant has migrated to a certain depth in the unsaturated zone, one may either analyze a sample of soil solution extracted from the desired depth or collect and analyze a sample of the soil collected at the desired depth. To better characterize mobility, analyzing a series of samples collected at a given depth is desirable, so that a plot of the change in concentrations with time can be developed. The collection of data at several depths over a period of time to determine the movement of the zone of maximum concentration is an even more effective method of mobility characterization. For the purpose of monitoring mobility below a land treatment facility, sampling is typically done at only one depth, i.e., the bottom of the treatment zone.

One unsaturated zone sampling system will not suffice for all purposes, since each has its limitations and advantages. As no presently available system is completely satisfactory, more reliable sampling methods must be developed and tested. The purpose of this paper is to gather and review information on existing and proposed methods of sampling the unsaturated zone.

PRESENT REGULATIONS AND GUIDANCE FOR UNSATURATED ZONE MONITORING AT HAZARDOUS WASTE LAND TREATMENT FACILITIES

The regulation requirements and permit guidance for soil and soil pore liquid samples were published in the Federal Register (1982) and by the EPA (1984), respectively. These are summarized in Table 1 for the soil samples and Table 2 for the soil pore liquid samples. The regulatory requirements for soil samples are general and give minimal details as to where or how many samples are to be collected. They do specify analysis for each hazardous constituent to be monitored. The permit writers' guidance document specifies that soil core samples are to be taken once in the background area and semiannually below the treatment facility from a zone within 15 cm of the bottom of the treated zone. Duplicate samples are composited to produce four from the background area and three samples per five hectares (ha) from the treatment facility. These samples are to be analyzed for the principal hazardous constituents.

TABLE 1. Comparison of regulations and guidelines on soil sampling.

	Background	Land Treatment Facility
	Regulatory Requirements	Federal Register Vol. 47 No. 143, July 26, 1982. (Ref. 8)
WHEN	One time sampling at a background plot having characteristics similar to those of the treatment zone	As specified by the regional administrator
WHERE	As required to represent chemical make up of background soil	As required to indicate chemical make up of soil below the treatment zone
HOW MANY	—	—
FOR WHAT	Each hazardous constituent to be monitored	Same
	Guidelines	Adapted from EPA 530-SW-84-016 (Ref. 7)
WHEN	Once	Semiannually
WHERE	Within 15 cm below treatment zone, i.e., 150-165 cm	Within 15 cm below treatment zone, i.e., 150-165 cm plus one from treatment zone for pH
HOW MANY	4*	3*/5 ha
FOR WHAT	Principal hazardous constituents	Principal hazardous constituents

*Each to be a composite of two samples in a uniform area.

TABLE 2. Comparison of regulations and guidelines on soil pore liquid sampling.

	Background	Land Treatment Facility
	Regulatory Requirements	Federal Register Vol. 47 No. 143, July 26, 1982. (Ref. 8)
WHEN	At least quarterly sampling for one year at a backbround plot having characteristics similar to those of the treatment zone	As specified by the regional administrator
WHERE	As required to represent the quality of background soil pore liquid	As required to indicate the quality of soil pore liquid below the treatment zone
HOW MANY	—	—
FOR WHAT	Each hazardous constituent to be monitored	Same
	Guidelines	Adapted from EPA 530-SW-84-016 (Ref. 7)
WHEN	Quarterly or "whenever liquid is present"	Quarterly or within 24 hrs significant of waste application
WHERE	Within 30 cm below treatment zone (150-180 cm)	Within 30 cm below treatment zone (150-180 cm)
HOW MANY	2	6/5 ha
FOR WHAT	Principal hazardous constituents	Principal hazardous constituents

While the regulations specify when samples of soil pore liquid and soil are to be taken and analyzed for each hazardous constituent, they do not give details as to where samples are to be taken, how many background samples are required, or what sampling methods are to be used (Table 2). The guidance document specifies that soil pore liquid samples are to be taken quarterly within 30 cm of the bottom of the treatment zone, with two samples required for background, six samples per five ha required for the treatment facility, and all samples to be analyzed for "Principal Hazardous" constituents.

Neither the regulations nor the guidance document gives details as to the acceptable methods for collecting soil or soil pore liquid samples. As will be seen later, this was likely a wise choice since there are still many problems and unknowns associated with the commonly available methods.

USE OF SOIL SAMPLES TO CHARACTERIZE THE UNSATURATED ZONE

Soil samples are best suited for determining the presence of contaminants that migrate slowly as a front through soil profiles. There is increasing evidence that in most structured soils, mobile constituents do not move in well defined fronts. Barbee and Brown (1985) reported that spilled xylene moved in a front only in very sandy soils; however, in clay loam and clay soils, migration occurred in the cracks and channels. Land treatment facilities are typically not installed in deep sandy soils because of the increased risk of migration of contaminants. Thus, most of the soils that would be sampled at the bottom of the treated zone would be expected to exhibit structural characteristics. Migrating chemicals are expected to be found only in or immediately adjacent to the cracks or large pores. Dye studies (Kissel et al. 1973; Anderson and Bouma 1977; Barbee and Brown 1985; and Brown et al. 1983) present visual evidence for the pattern of movement through structured subsoil. If a soil sample is taken from the center of a soil structure, the presence of a contaminant may be entirely missed. If a sample intercepts a conducting channel, the presence of the contaminant should be evident in an analysis but will likely exceed the average concentration of the contaminant at that depth. In order for soil samples to provide adequate data on the presence of mobile constituents, either replicate samples must be taken, which could be composited; or single samples large enough to include a representative cross section of the structural units are needed. Even this procedure may not be entirely satisfactory, since it is possible that if contaminants occur in low concentrations, they will be further diluted by the soil inside the soil structure (peds) and result in concentrations below the detection limits. An additional difficulty is the scant available information in the literature on the size of sample required to be representative. Bouma and Dekker (1978) investigated the frequency of the spacing of cracks in the soil and reported that conductive channels occurred in a clay soil in a rather regular pattern at a spacing which averaged 62.5 cm^2. This large spacing suggests that samples much larger than those normally taken would be required.

In addition to the problems associated with collecting a representative sample on a scale of the peds, the additional problem exists of collecting representative samples of the different units of soil that may occur within a given facility.

A detailed soil survey should assist with decisions as to where and how many samples may be needed. Even then, however, unmapped inhomogeneities may result in a broad range of soil characteristics, and different hydraulic conductivities may have an impact on the transport of contaminants (Nielsen et al. 1973). Such inhomogeneities in soil properties will have an impact on the spacing of both soil and soil pore liquid samples needed to characterize the flow of leachate and possible contaminants toward the groundwater.

A thorough description of the sampling equipment needed to collect soil samples, including hand augers and power driven equipment, has been presented by the EPA (1984). Two additional considerations are the need to take precautions against possible cross contamination between soil samples taken from different layers and the need to refill the sampling holes to prevent short circuiting of runoff or leachate following sampling. Cross contamination is a particularly troublesome problem when the surface horizon is highly contaminated with waste and is of a loose and friable nature. To prevent this soil from falling down the sampling hole and contaminating lower samples, it is often desirable to remove the contaminated soil for some distance around the sampling hole and surround the sampling hole with a pipe or container that is open on both ends.

Care must be taken to repack sampling holes with clean fill. It may be desirable to use bentonite to fill bore holes. The different color and texture of bentonite should also serve to label the sampling location and minimize the possibility of a later sample being taken in the same location.

Soil Pore Water Samplers

A variety of soil pore water samplers have been utilized to collect liquids moving through unsaturated soil. These devices may be divided into two groups; 1. those consisting of porous membranes with bubbling pressure greater than the vacuum applied, and 2. free drainage samplers that depend on gravity drainage to a collection pan or trough. Typical systems for collecting samples from porous cups are shown in Figure 1. They consist of either continuous vacuum, intermittent vacuum, or a vacuum extraction and are followed by the application of pressure to drive the sample from the cup to a collection chamber.

While suction samplers have been widely used, many researchers have identified problems with their use. Wagner (1962) reported that ceramic cups have an adsorption capacity for ammonia, thus distorting the concentrations in the collected samples. This was confirmed by Zimmermann et al. (1978), who found that ceramic cups passed 112% and 43% of the NH_4 and PO_4^{3-}, respectively, in the initial solution. Zimmermann et al. (1978) reported 102% and 106% recovery of NH_4 and PO_4^{3-}, respectively, from the initial solution when porous teflon cups were used. Porous teflon samplers have the disadvantages of not being generally available at the present time and the difficulty of maintaining uniform pore size during manufacture. In a study on phosphorus adsorption, Nagpal (1982) reported that the phosphorus adsorption by ceramic cups was a reversible reaction and was dependent on the solution concentration. Since the pore size from which water is extracted by suction cups and the volume of soil from which the sample is extracted is unknown, Van der Ploeg and Beese (1977) suggested that

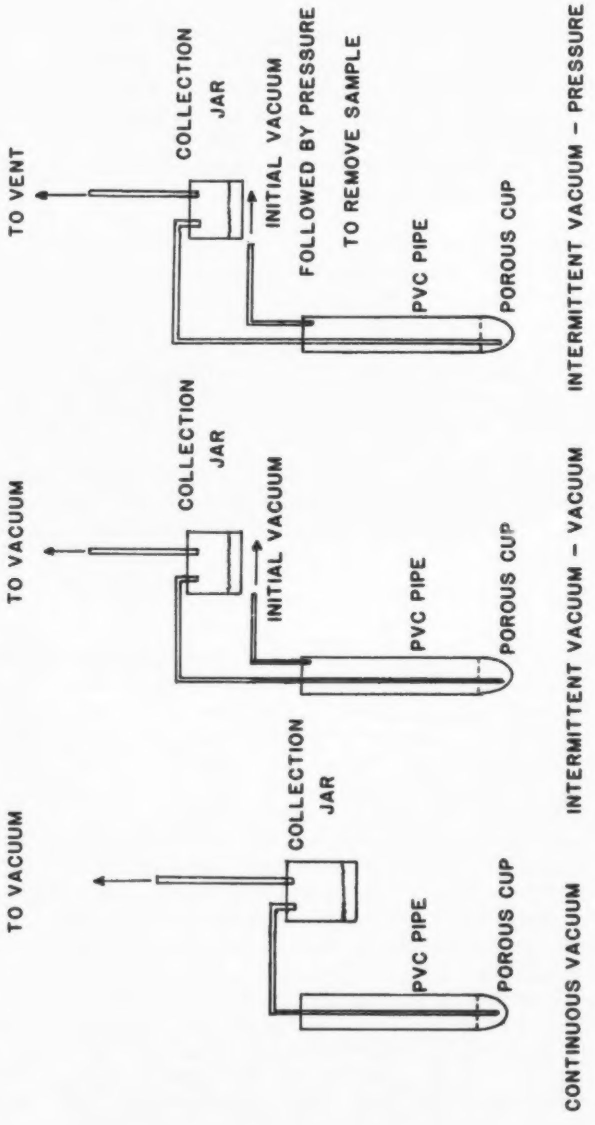
TO VACUUM
COLLECTION JAR
PVC PIPE
POROUS CUP
CONTINUOUS VACUUM
TO VACUUM
COLLECTION JAR
INITIAL VACUUM
PVC PIPE
POROUS CUP
INTERMITTENT VACUUM – VACUUM
TO VENT
COLLECTION JAR
INITIAL VACUUM
FOLLOWED BY PRESSURE
TO REMOVE SAMPLE
PVC PIPE
POROUS CUP
INTERMITTENT VACUUM – PRESSURE

FIGURE 1. Three typical systems used for collecting samples from porous cups.

there is no useful relationship between the amount and concentration of chemicals in samples collected via suction cups and the water that is percolating through the soil.

Volatile chemicals collected by vacuum in porous cups will likely be lost before the sample can be retrieved. Barbee and Brown (1985) reported large losses of xylene from soil solution samples collected when a vacuum was applied to collect samples for even as short a time as 15 minutes. Although free xylene was found in the pan lysimeters, the concentrations found were not in excess of the solubility of xylene in water in the suction cup samplers. They also showed that xylene vaporizes from water under a vacuum when the concentrations are greater than the solubility.

Suction cups are also prone to failure in that no sample is typically collected. Silkworth and Grigal (1981) reported that 31% of their 4.8 cm diameter and 51% of the 2.2 cm diameter cups failed after two weeks of suction. Barbee and Brown (1986) reported that the 2.2 cm cups routinely provided samples in sand and loam soils but failed to provide adequate samples in clay soils. In other studies conducted by this author, ceramic cups have provided adequate samples in medium and coarse textured soils for several years, provided the soils were not calcareous. In calcareous soil, periodic flushing of the cups with a dilute hydrochloric acid (HCl) solution was necessary.

Suction cups offer some limited advantages. These are summarized in Table 3 and include ease of installation, ability to sample unsaturated soil, and good performance under saturated conditions. The usefulness of the collected data, however, is questionable.

Pan Lysimeters

Pan lysimeters have been used by Haines et al. (1982), Barbee and Brown (1985 and 1986) and others. These typically consist of a tray, funnel, or glass container buried in the soil at the desired depth. They vary in collection cross section from 10 to 30 cm. A diagram of a pan sampler made from a commercially available glass block, as described by Barbee and Brown (1985), is shown in Figure 2. Theoretically, soil solution should drain into these samplers only when the soil is saturated. However, field experience by Haines et al. (1982), Barbee and Brown (1985) and others indicate that samples are often easily collected in pan lysimeters. A large part of this liquid may result from unsaturated flow through macropores (Bouma and Dekker 1978). Pan lysimeters often do not function well in sandy soils but do provide adequate samples in finer textured soils, particularly clay soils, in which much of the water movement may take place in a few large pores.

Free drainage samplers collect the rapidly moving water but provide no data on the flux of water. It is likely that the concentration of salts and organic contaminants would not be altered by these devices if the materials used in their construction are carefully selected. However, no information is available on how representative the sample is of the water moving past a particular depth. The data of Barbee and Brown (1985) and Shaffer et al. (1979) indicate that chemical concentrations measured in pan lysimeters may be as much as one to three orders of

TABLE 3. Advantages and disadvantages of soil pore water sampling methods.

	Method			
Types of Performance	Porous Cup	Pan Sampler	Barrel Lysimeter	Wick Sampler
Ease of Installation	Easiest	Intermediate	Most difficult	Intermediate
Ability to Sample Unsaturated Soil-Pores	Yes	No	Yes	Yes
Ability to Sample Saturated Soil-Pores	Yes	Yes	Yes	Yes
Ability to Sample Cross Sectional Macro-Pores	Minimal to none	Intermediate	Excellent	Intermediate
Disturbance to Soil Profile Above Sample Point	Moderate	Moderate	Minimal	Moderate
Reliability of Sample to Represent Actual Condition	Questionable	Good	Excellent	Good
Effort Required to Obtain Samples and Maintain Devices	Intermediate	Low	High	Low
Performance Under Saturated Conditions	Good	Good	Good	Good
Performance Under Unsaturated Conditions	Fair	Fair-Poor	Good	Good
Possibility of Providing Data on flux	None	Fair	Good	Possibly good

magnitude greater than those from porous cup samplers. Additional advantages and disadvantages are listed in Table 3.

Barrel Lysimeters

Lysimeters have been used by researchers to monitor the movement of water and nutrients through soils. Recent advances now allow the procurement of barrel sized undisturbed soil monoliths (Brown et al. 1985). Briefly, these lysimeters consist of a round metal casing surrounding an undisturbed monolith.

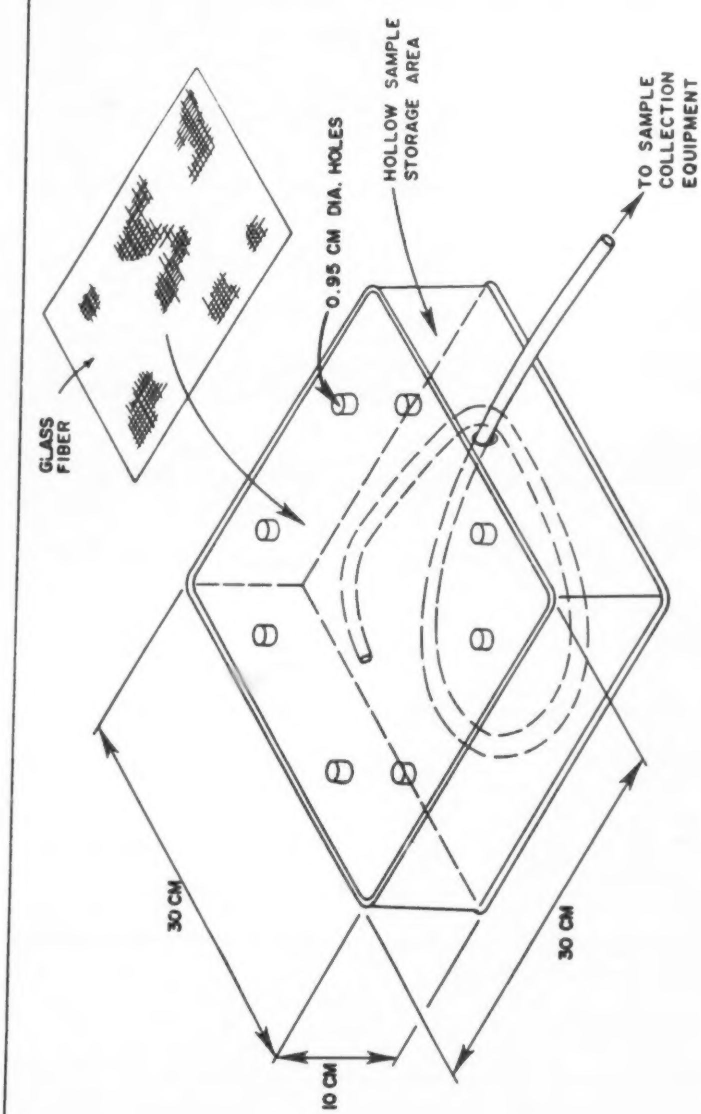
GLASS FIBER
0.95 CM DIA. HOLES
HOLLOW SAMPLE STORAGE AREA
TO SAMPLE COLLECTION EQUIPMENT
30 CM
30 CM
10 CM

FIGURE 2. Schematic diagram of a pan sampler made from a glass block.

Porous ceramic cups are installed in the bottom of the monolith, and a watertight bottom is sealed on the casing. By drilling a 60 cm diameter hole to the desired depth, the lysimeter can be placed below the soil surface, as pictured in Figure 3. Leachate from the overlying surface soil will be intercepted by the lysimeter and sampled when it reaches the porous cups.

While this method is more costly and difficult to install, it has several advantages: (1) Barrel lysimeters have an average surface area of about 2800 cm^2; (2) They can sample both saturated and unsaturated flow through soil; and (3) They can provide an accurate estimate of soil water flux. If the lysimeters are properly installed, normal tillage operations can be done without any skirting of the sample area. Among the primary criticisms of lysimeters is the use of porous cups to sample the leachate; however, some of the problems associated with porous cups are alleviated when used in a confined volume. While adsorption/desorption of chemicals onto the ceramic remains a problem, measurement of both macropore flow and soil water flux is possible. Data collected from barrel lysimeters should accurately represent field conditions. Neither the exact number of necessary lysimeters per unit land area nor the useful lifetime of such lysimeters has been determined. The use of barrel lysimeters in field situations requires a higher level of maintenence and daily activity than do some of the other samplers.

Wick Sampler

The wick sampler represents an attempt to combine the advantages of both the porous cup and pan samplers. A diagram of a wick sampler is shown in Figure 4. The wick sampler consists of a glass plate with a hole in the center through which a glass wick extends. The wick is frayed above the plate to cover the plate surface and enclosed in a tube below the plate, which extends to a collection vessel at a given depth below the plate. While the samplers can be made with various surface areas, there is no documentation as to what area is necessary for specific soil types.

Gravitational water will be intercepted by the plate and drawn through the wick into the collection vessel. The water within the wick will act as a hanging water column to draw water from moist unsaturated soil above the plate. This sampler has the potential to sample both saturated and unsaturated soil; however, there is no documentation of the exact soil moisture potential range in which the sampler is effective. A summary of the advantages and disadvantages of the wick sampler is given in Table 3.

A considerable data base is still needed to document the performance of this sampler. The three main problems that need to be addressed are: (1) An evaluation of the fraction of flowing water that is sampled by a wick sampler; (2) Determination of the number and size of samplers needed at any given location to obtain representative samples; and (3) An evaluation of the adsorption/desorption of leachate constituents on the wick material. It is anticipated, however, that the adsorption/desorption of constituents will be minimal through proper selection of materials. A thorough investigation of the performance of wick and other types of samplers is in progress.

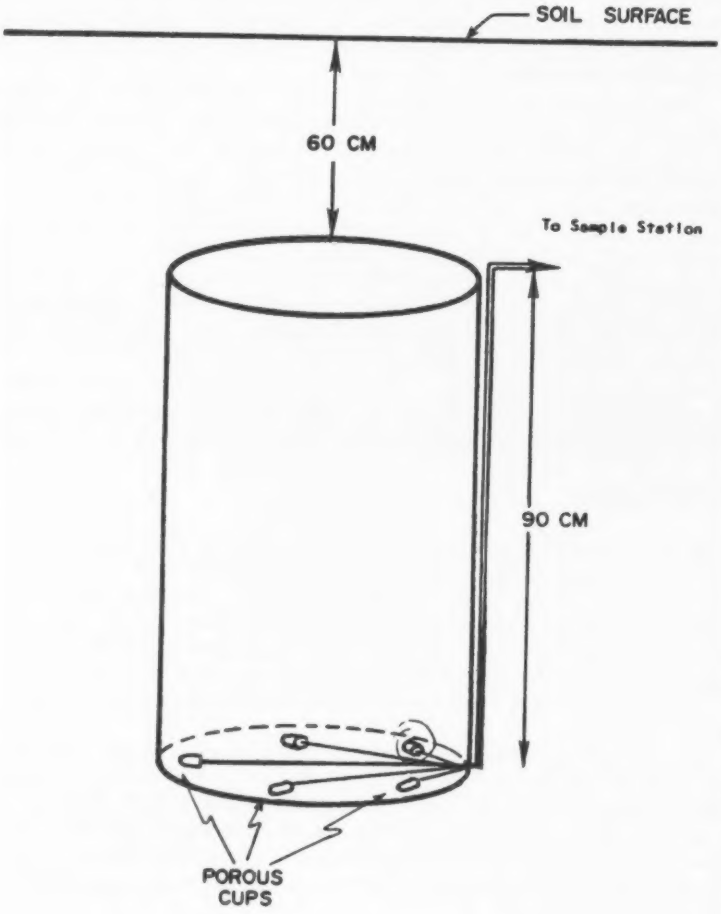
SOIL SURFACE
60 CM
To Sample Station
90 CM
POROUS CUPS

FIGURE 3. A barrel lysimeter installed 60 cm below the soil surface.

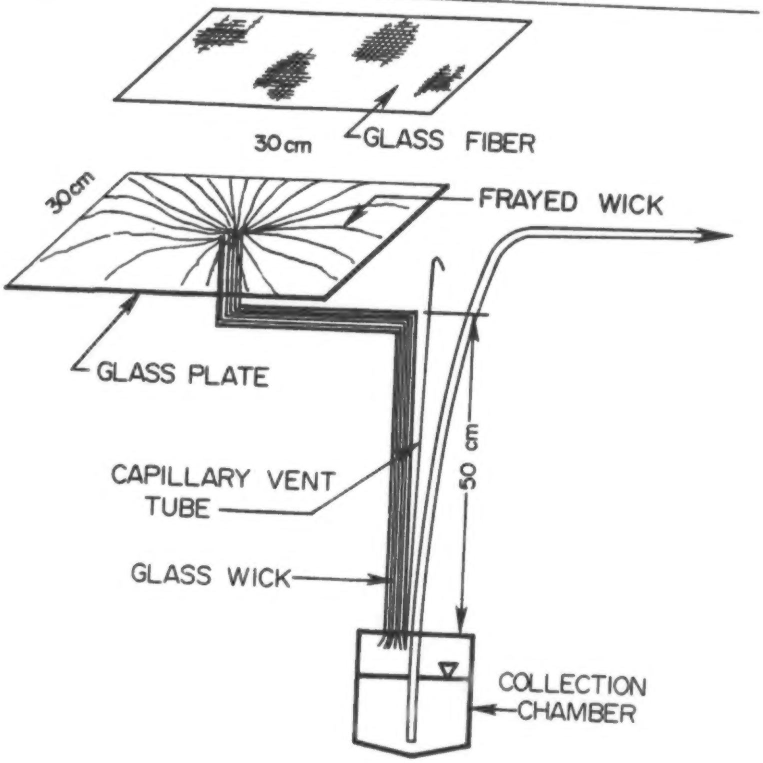
30cm
GLASS FIBER
30cm
FRAYED WICK
GLASS PLATE
CAPILLARY VENT TUBE
GLASS WICK
50 cm
COLLECTION CHAMBER

FIGURE 4. Schematic diagram of a wick sampler.

SUMMARY

Each of the techniques described herein for sampling the unsaturated zone has one or more flaws which need to be overcome or need further development before they can be used with full confidence. The question as to the size, type, or number of samplers needed to provide a representative sample remains unresolved. There is also little guidance available as to the time period over which samples should be drawn or the frequency with which they should be taken to represent the concentration of contaminants flowing through the soil. Information is also generally lacking on the useful life of any of the described sampling devices, although the useful life of porous cups is likely less than that of pan and wick samplers, particularly in calcareous soils. Barrel lysimeters will probably be limited to the lifetime of the casing or the porous cups, whichever is least. Continued research is needed to improve our ability to accurately sample and monitor the unsaturated zone.

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GROUNDWATER MONITORING NEEDS IN THE SATURATED ZONE

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ABSTRACT

The spreading of industrial hazardous wastes on land may result in the treatment, short-term immobilization, or dilution of the chemical components of the waste mixtures. There is very little known about the long-term environmental consequences of land spreading and the migration of waste constituents or treatment by-products beyond the treatment zone. It is clear that efforts to monitor the progress of treatment or migration processes in the shallow subsurface or vadose zone may increase the potential for groundwater contamination. Regulations based on concentrations of original waste components will probably not be sufficiently protective of the environment, since the treatment and weathering processes can cause substantial changes in inorganic speciation and organic breakdown product distributions.

From this point of view, a well-conceived groundwater monitoring program should be implemented at land spreading sites. The development of sampling and analytical protocols should follow a thorough hydrologic evaluation of site conditions. In order to most effectively choose the chemical constituents which may be indicators of potential groundwater contamination, the results of long-term column microcosm or soil/waste admixture leaching experiments may be useful.

INTRODUCTION

Land farming, cultivation, or spreading of hazardous industrial wastes by design has been practiced as an alternative to landfilling for at least twenty years. Many authors have pointed out the inherent difficulties involved in the secure disposal of industrial wastes by landfilling. The pitfalls involved in landfilling stem from the difficulties involved in assuring secure waste retention and the generation of contaminant-laden leachate under anaerobic conditions within the fill material. When waste materials are placed in the soil, they are susceptible to four principal fates as a result of physical, chemical, and microbial processes: (1) Decomposition of organic materials; (2) Leaching of soluble waste constituents and by-products; (3) Volatilization of gaseous waste constituents and by-products; (4) Accumulation of waste residues in the soil matrix. The consequences of these processes have been studied only in a very superficial manner. Obviously, when the "natural" treatment and remineralization capabilities of the soil, so-called "assimilative capacity," are exceeded by the waste loading, the potential exists for the long-term contamination of the soil and groundwater. The potential groundwater impacts of overloading land treatment systems with industrial wastes or municipal sewage sludge should be clearly recognized by the scientific community as a likely result of the choice of this least expensive short-term waste management option. The gravity of these impacts scarcely needs recounting and has been recognized for a long time (Lazar et al. 1976).

Published literature on land spreading frequently alludes to the treatment process as a physical/chemical/biological waste treatment method that uses the natural capacity of the soil system to degrade, assimilate, and immobilize certain waste constituents (Berkowitz et al. 1983a; Morrison 1983; Ross and Phung 1978). It is notable among much of this published work that the terms treatment and disposal are used interchangeably, although little verification of treatment or disposal efficiency has been forthcoming. The lack of groundwater quality monitoring data is particularly clear in available reviews (Berkowitz et al. 1983a). Despite the growing public awareness of the vulnerability of our groundwater resources and technical references which call for a systematic screening of hazardous industrial wastes prior to land treatment (Brown et al. 1980), a literature-review screening process has been proposed which ranks candidate waste streams on a limited basis (Berkowitz et al. 1983b). Much of this proposed screening process is predicated on the availability of data on waste stream composition and information from the literature on the reactivity or physical properties of waste constituents or soil matrix properties. Soil pH and cation-exchange capacity have been recognized as poor measures of "assimilative" capacity for inorganic waste constituents for some time (Ryan 1976). Organic waste constituents, by the same token, exhibit a diverse array of sorption, transformation and transport properties which are quite difficult to predict with certainty from the literature data (Cohen et al. 1984: Dragun and Helling 1982). Indeed, even for waste streams amenable to soil treatment, a reasoned approach for screening candidate wastes must include careful consideration of the fate and mobility of waste constituents and the potential by-products of the "treatment" processes (K. W. Brown et al. 1983).

Regulations governing the operation and monitoring of land treatment units require that a degree of efficiency or performance be established (USEPA 1982a, 1983; Everett and Wilson 1983). It must be recognized, however, that the soil and groundwater environments are complex biogeochemical systems which may assimilate or dissimilate waste residuals in a correspondingly complex fashion. Regulating the original waste constituents on the basis of eluent concentrations from open microcosm or short-term leaching studies ignores the potential for damage to the environment and human health (NAS 1977; Harris et al. 1980) because hazardous waste degradation and transformation products that may be present are overlooked.

It is essential that the plans for the operation and monitoring of sites for land spreading of hazardous wastes provide a verifiable degree of assurance that the unit will either obviate long-term environmental deterioration or mitigate such effects. Vadose zone monitoring should provide early detection of potentially serious problems if it is approached properly. In order for saturated zone monitoring to have real effectiveness for detective and assessment efforts, vadose zone monitoring activities should be carefully planned and coordinated so as to avoid "short-circuiting" the treatment zone approach called for in the regulations. The need for groundwater monitoring at land spreading sites is then ultimately the same as that required at landfilling or cleanup/remedial action sites. The advantage is that unsaturated zone monitoring may provide an early warning which may spur assessment monitoring activities.

PLANNING AN EFFECTIVE GROUNDWATER MONITORING PROGRAM

Purpose and Needs

Monitoring activities at hazardous waste land treatment facilities are required for several purposes: to assess the efficiency of the soil processes which degrade waste materials, to detect the migration of hazardous constituents beneath the treatment zone (i.e., 1.5 m below initial land surface and within 1.0 m of the seasonal high water table) and to permit an adequate assessment of the long-term efficiency of facility operations.

In order to meet these objectives with a well-conceived and executed monitoring program, the owner/operator must collect sufficient supporting data on the physiography, hydrology, and treatment capacity of the site. Runon and runoff control, as well as waste loading and fertilizer amendment needs for balanced soil treatment, should be an implicit part of the effort. A water balance and some historical data on precipitation and groundwater levels are also needed. It should be clear that the successful operation of the site should include thorough waste treatment pilot studies and that the subsurface monitoring installations should be effectively located and constructed to withstand time, as well as the operation of heavy equipment. A competent surveyor should certify the location of these installations. In the planning stages, it should be kept in mind that disturbance of the soil profile by trenching, boring, or well construction can provide avenues for the rapid migration of mobile chemical constituents. All installations should therefore be very carefully documented. These supporting data, collected during the site planning process, also permit an identification of the quality assurance/control measures which will insure that the documentation of the facility's operation is sufficient for future needs (Sisk 1981; Brown and Black 1983). Once initial planning has occurred, the saturated zone monitoring activities at a hazardous waste land treatment unit are very similar to those of any waste management facility. Groundwater monitoring is an important facet of operation, given that the treatment zone may extend to within 1.0 m of the seasonal high water table and that the owner/operator must determine if statistically significant increases in hazardous constituents have occurred below the treatment zone.

The practical elements of a viable long-term groundwater monitoring effort include: (1) Evaluation of hydrogeologic setting and program information needs; (2) Proper well placement and construction (both method of drilling and well drilling materials); (3) Evaluation of well performance and purging strategies; (4) Execution of effective sampling and analytical protocols which entails appropriate selection of sampling mechanisms and materials, as well as sample collection, handling, and analytical procedures. All of these elements are described in detail in several published guides for groundwater monitoring efforts (Scalf et al. 1981, Barcelona et al. 1983, Barcelona et al. 1985).

Hydrogeologic Setting and Information Requirements

The hydrogeologic conditions at each site (e.g., background and regulated unit) must be evaluated for the potential impacts that the setting may have on the development of the monitoring program and the quality of the resulting data (Eccles and Nicklen 1978). The types and distribution of geologic materials, the occurrence and movement of groundwater through those materials, the location of the site in the regional groundwater flow system, the relative permeability of the materials, and the potential interactions between the mineral and biological constituents of the formations of interest and the waste constituents must all be considered. Both the direction and the rate of groundwater movement are important. Piezometric surface data or water level information of each geologic formation at properly selected locations will provide the basis for determining horizontal and vertical groundwater flow paths at the site. There are significant differences between the hydrogeology of arid and humid climatic regions, as well as seasonal variations which should be taken into account. The rate of groundwater travel can be used to calculate reasonable sampling frequencies, should additional detail beyond that provided in quarterly sampling become necessary. Land treatment operations may be considered potentially large (5 acres) point-sources of groundwater contamination. If however, wastes are unevenly applied, spilled and sampling point installations provide a conduit for localized waste constituent migration; the facility may act as a local source.

Additional site and waste information needs arise when tailoring the sampling and analytical protocols to the specific needs of the program. A minimum data set for groundwater monitoring should include general water quality parameters, hydrologic parameters, and pollutant indicator parameters. A suggested list of basic measurements is provided below:

Chemical Parameters	**pH, Ω^{-1} (conductance), TOC, TOX** **Alkalinity, Cl^-, NO_3^-, $SO_4^=$, $PO_4^\equiv$, Silicate** **Na^+, K^+, Ca^{++}, Mg^{++}, Fe and Mn**
Hydrologic Parameters	Water level, hydraulic conductivity

The pollutant indicator parameters noted above (i.e., pH, Ω^{-1}, TOC and TOX) provide minimal capability to insure the detection of hazardous constituents which migrate beyond the treatment zone. The pH and conductance parameters should be measured with care in the field. TOC and TOX determinations should be made after collection in headspace free glass vials with Teflon(R) septa so as to preserve the volatile organic fraction of the dissolved organic matter. The pollutant indicator parameters should also be supplemented with determinations of hazardous constituents in the wastes or waste treatment by-products which have been identified in treatment evaluation pilot studies.

Well Placement and Construction Procedures

The placement and construction of monitoring wells are among the most difficult tasks involved in developing an effective monitoring program. The preliminary locations and depths of monitoring wells should be selected on the basis of the best available predrilling information. Then, as the installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan to insure that the wells will perform the tasks for which they are designed. It is probably advisable to initially select a minimum array of monitoring wells for the collection of geologic and hydrologic data. Additional wells can be positioned later at monitoring points likely to intercept the contaminant flow path.

Well construction should be accomplished with minimal disturbance of the subsurface. The selection and cleaning of both drilling equipment and well construction materials should be performed with the aim of minimizing the introduction of foreign materials into the subsurface environment (Barcelona et al. 1983, Barcelona et al. 1985). Given the relatively shallow depths of interest in land treatment monitoring efforts, hollow-stem auger drilling techniques are preferred as they are mobile, fast, and inexpensive. Also, disturbance of the subsurface can be effectively minimized. To properly define the movement of pollutants in both vertical and horizontal directions, it is essential to collect depth-discrete water level data. Well completion depth will depend on the location of the uppermost permeable, saturated zone (i.e., "water-table") in unconfined formations or the piezometric surface of the most shallow permeable zone in confined formations. Vertically nested wells provide information on the vertical direction of groundwater movement, and their placement will be a function of the hydrogeologic setting, particularly the relative horizontal and vertical permeabilities of the formations beneath the site. Screen size, grouts, seals, and sampling point documentation are also important aspects of monitoring well construction which should be addressed in the monitoring program.

Evaluation of Well Performance

The effectiveness of a groundwater monitoring program may be judged on the attention which has been paid to the evaluation of the hydraulic performance of the monitoring well network. Each well should be properly developed after construction and periodically redeveloped to insure that it provides useful hydraulic data. Development also reduces the time and effort necessary to collect representative groundwater quality information from filtered water samples. A variety of well development techniques are amenable to the development of shallow 2″ outside diameter monitoring wells. Accurate water level measurements provide the primary data for the evaluation of well performance. Steel tapes (graduated to the nearest hundredth of a foot with raised lettering and divisions), electrical drop lines, and sensitive pressure transducers are useful tools in this regard.

Field hydraulic conductivity testing of the monitoring wells will avoid the unresolved issues which attend the interpretation of laboratory conductivity test results. Slug or bail tests, repeated at least three times, should provide accurate hydraulic conductivity determinations with a precision of ±20%. In general, multiple pump tests are too expensive to consider for evaluating the hydraulic performance of all monitoring wells within a site network. The results of conductivity tests provide a basic measure of well hydraulic performance which is useful for judging the significance of water level excursions and long-term well performance. The testing procedures should be repeated at least every five years and after each redevelopment effort is performed to remove accumulated sediment from the wells. Well performance evaluation also provides a basis for determining an appropriate well purging strategy prior to sampling. No single number of purge volumes to be pumped prior to sampling representative groundwater can be expected to suit all situations (Gibb et al. 1981). A well-conceived purging strategy, which includes pumping rates and volumes calculated on the basis of well performance and the transmissivity of the formation of interest, is essential to effective groundwater sampling efforts.

Sampling and Analytical Protocols

The hydraulic performance of the sampling points permits the design and execution of effective water sampling and analytical protocols. These protocols should be planned for the collection of verifiable, high-quality water chemistry results in order to distinguish natural variability in the geochemistry of the land treatment operation from those caused by site operations. The sampling protocol should incorporate sampling mechanisms and materials which are appropriate for the information needs of the program. Since hazardous waste migration may be detected at trace (e.g., ppb) levels of individual constituents, sampling mechanisms and materials must be very carefully chosen (Barcelona et al. 1983) to avoid biases caused by contamination or sorption. The materials of well construction, samplers, and sample transfer tubing are equally important as are sample storage vessels and analytical performance in this respect. Recommended materials for well construction and sampling devices are shown in Tables 1 and 2. Materials selections should be made with the long-term use of the sampling points in mind (Barcelona et al. 1985).

Sampling mechanisms are devices for the collection of water samples. They are not, of themselves, sampling methods. This should be clear from inspection of Figure 1. The steps in the sampling protocol in the first column of the figure are common to all groundwater monitoring efforts. Though the details of individual monitoring efforts may vary, the steps in the figure provide a guide for effective planning. The performance of the sampling point, materials selection,

TABLE 1. Recommendations for rigid materials in sampling applications (in decreasing order of preference).

Material	Recommendations
Teflon (R) (flush threaded)	Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions. Virtually an ideal material for corrosive situations where inorganic contaminants are of interest.
Stainless Steel 316 (flush threaded)	Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions.
Stainless Steel 304 (flush threaded)	May be prone to slow pitting corrosion in contact with acidic high total dissolved solids aqueous solutions. Corrosion products limited mainly to Fe and possibly Cr and Ni.
PVC (flush threaded) other noncemented connections, only NSF* approved materials for well casing or potable water applications	Recommended for limited monitoring situations where inorganic contaminants are of interest and it is known that aggressive organic leachate mixtures will not be contacted. Cemented installations have caused documented interferences. The potential for interaction and interferences from PVC well casing in contact with aggressive aqueous organic mixtures is difficult to predict. PVC is not recommended for detailed organic analytical schemes.
	Recommended for monitoring inorganic contaminants in corrosive, acidic inorganic situations. May release Sn or Sb compounds from the original heat stabilizers in the formulation after long exposures.
Low-Carbon Steel Galvanized Steel Carbon Steel	May be superior to PVC for exposures to aggressive aqueous organic mixtures. These materials must be very carefully cleaned to remove oily manufacturing residues. Corrosion is likely in high dissolved solids, acidic environments, and particularly when sulfides are present. Products of corrosion are maninly Fe and Mn, except for galvanized steel which may release Zn and Cd. Weathered steel surfaces present very active adsorption sites for trace organic and inorganic chemical species.

(R) Trademark of DuPont, Inc.

* National Sanitation Foundation approved materials carry the NSF logo indicative of the product's certification of meeting industry standards for performance and formulation purity.

and the analytical parameters of interest will dictate the choice of appropriate sampling devices. Figure 2 contains recommendations for sampling mechanisms according to the specific demands of the monitoring effort.

Land treatment facilities will have particularly stringent analytical constraints. Since the aim is treatment and containment of hazardous waste constituents, as well as the treatment by-products; there are potentially many analytical parameters of interest in detective monitoring efforts. Within this format, it would be impossible to even speculate on specific analytical needs and agency recommendations that should be followed (EPA 1982b).

TABLE 2. Recommendations for flexible materials in sampling applications (in decreasing order of preference).

Materials	Recommendations
Teflon$^{(R)}$	Recommended for most monitoring work, particularly for detailed orgainic analytical schemes. The material least likely to introduce significant sampling bias or imprecision. The easiest material to clean in order to prevent cross-contamination.
Polypropylene Polyethylene (linear)	Strongly recommended for corrosive high dissolved solids solutions. Less likely to introduce significant bias into analytical results than polymer formulations (PVC) or other flexible materials with the exception of Teflon$^{(R)}$.
PVC (flexible)	Not recommended for detailed organic analytical schemes. Plasticizers and stabilizers make up a sizable percentage of the material by weight as long as it remains flexible. Documented interferences are likely with several priority pollutant classes.
Viton$^{(R)}$ Silicon (medical grade only) Neoprene	Flexible elastomeric materials for gaskets, O-rings, bladder and tubing applications. Performance expected to be a function of exposure type and the order of chemical resistance as shown. Recommended only when a more suitable material is not available for the specific use. Actual controlled exposure trials may be useful in assessing the potential for analytical bias.

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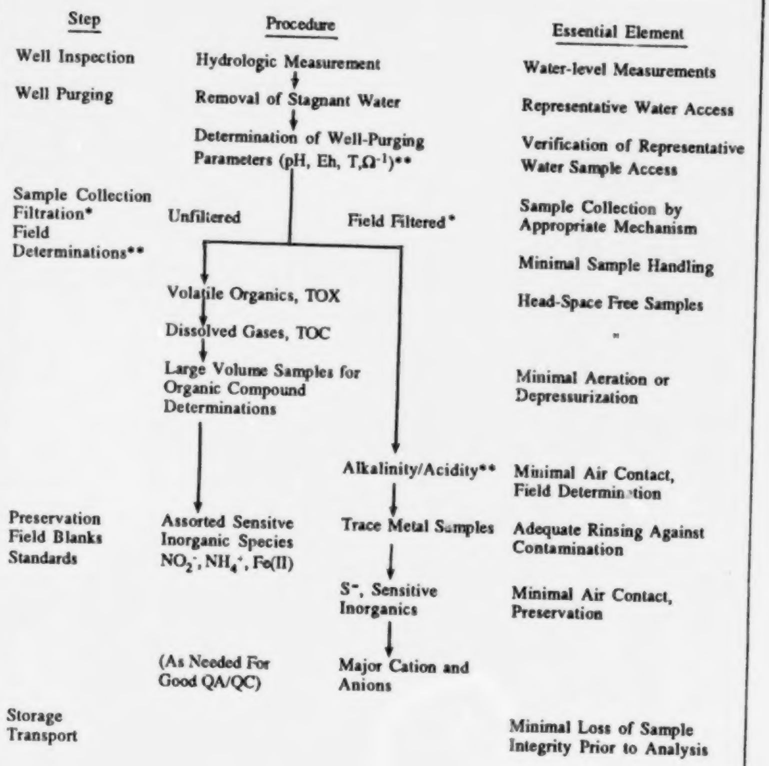
Step
Procedure
Essential Element
Well Inspection
Hydrologic Measurement
Water-level Measurements
Well Purging
Removal of Stagnant Water
Representative Water Access
Determination of Well-Purging Parameters (pH, Eh, T,Ω-1)**
Verification of Representative Water Sample Access
Sample Collection
Filtration*
Field Determinations**
Unfiltered
Field Filtered*
Sample Collection by Appropriate Mechanism
Minimal Sample Handling
Volatile Organics, TOX
Head-Space Free Samples
Dissolved Gases, TOC
"
Large Volume Samples for Organic Compound Determinations
Minimal Aeration or Depressurization
Alkalinity/Acidity**
Minimal Air Contact, Field Determination
Preservation
Field Blanks
Standards
Assorted Sensitve Inorganic Species NO2-, NH4+, Fe(II)
Trace Metal Samples
Adequate Rinsing Against Contamination
S=, Sensitive Inorganics
Minimal Air Contact, Preservation
(As Needed For Good QA/QC)
Major Cation and Anions
Storage
Transport
Minimal Loss of Sample Integrity Prior to Analysis

* Field filtration should be done by pressure (e.g., flow or inert gas) not vacuum technique for inorganic species, alkalinity/acidity. Samples for organic compound determinations should not be filtered (e.g., especially volatile organics) unless absolutely necessary. In these cases, laboratory pressure filtration is preferred for the other organic constituents to avoid loss or contamination.

**Denotes parameters which should be determined in the field.

FIGURE 1. Generalized flow diagram of groundwater sampling steps.

Type of Constituent	Example of Constituent		Positive Displacement Bladder Pumps	Thief, In Situ, or Dual Check Valve Bailers	Mechanical Positive Displacement Pumps	Gas-Drive Devices	Suction Mechanisms
			← INCREASING RELIABILITY OF SAMPLING MECHANISMS				
Volatile Organic Compounds	Chloroform TOX CH_3Hg	INCREASING SAMPLE SENSITIVITY	Superior Performance	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Organometallics							
Dissolved Gases	O_2, CO_2		For	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Well-Purging Parameters	pH, Ω^{-1} Eh						
Trace Inorganic Metal Species	Fe, Cu		Most	May be adequate if well purging is assured	Adequate	May be adequate	May be adequate if materials are appropriate
Reduced Species	NO_2^-, $S^=$						
Major Cations & Anions	Na^+, K^+, Ca^{++} Mg^{++}		Applications	Adequate	Adequate	Adequate	Adequate
	Cl^-, SO_4^-			May be adequate if well purging is assured			

FIGURE 2. Matrix of sensitive chemical constituents and various sampling mechanisms.

CONCLUSIONS

Land treatment units have a regulatory need to closely monitor all aspects of site operation. Treatment efficiency and the containment of both waste constituents and treatment by-products in the biogeochemical treatment zone must be engineered into the planning and operation of these facilities.

The details of effective groundwater monitoring activities at land treatment facilities should be planned specifically for the site of interest. The demands on the monitoring systems at such facilities are particularly critical where shallow, unconfined aquifers may be impacted by potential contaminant release.

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TREATMENT DEMONSTRATION PROTOCOL FOR LAND TREATMENT UNITS

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INTRODUCTION

Most evaluations of national hazardous waste management strategies are today identifying and focusing upon the weaknesses of traditional land disposal options. Alternatively, methods that emphasize recycling, volume reduction, and treatment are correctly being lauded as the preferred approaches when possible. Land treatment, among the land disposal technologies, can effectively perform the volume reduction and treatment functions sought while operating in an environmentally safe fashion. Figure 1 illustrates the prominent place occupied by land treatment in a reasoned waste management strategy.

The effectiveness of land treatment has been practically demonstrated via research and industrial activities for a wide variety of wastes, most notably oily refinery wastes, and environmental settings. Nevertheless, prudent use of the technology requires that suitable measures be taken to ensure unit performance in specific cases. The success of any given operation is influenced by the combined effects of site, waste(s), design, construction, operation, and monitoring. Therefore, from the perspective of the industrial user, a performance demonstration serves as insurance against potential long-term health and environmental damages and the associated economic liabilities. The regulatory agencies have likewise endorsed this need for a treatment demonstration in their final issuance of standards.

The question that remains is what constitutes a land treatment demonstration (LTD) and how much or little (depending upon your perspective) information is adequate to reach defensible conclusions? The draft Environmental Protection Agency (EPA) guidance document "Hazardous Waste Land Treatment Demonstrations" (1) was formulated to provide the facility owner/operator and agency permit writer with practical answers to this question. This discussion is based on the information found in that document, with the objective of putting the LTD in perspective, briefly examining the major elements of an LTD, and illustrating the practical application of these elements.

One might ask how extensive an LTD should be and how confident we need to be of the treatment demonstration results? For new or poorly documented sites or wastes not previously land treated, relatively extensive proofs may be in order.

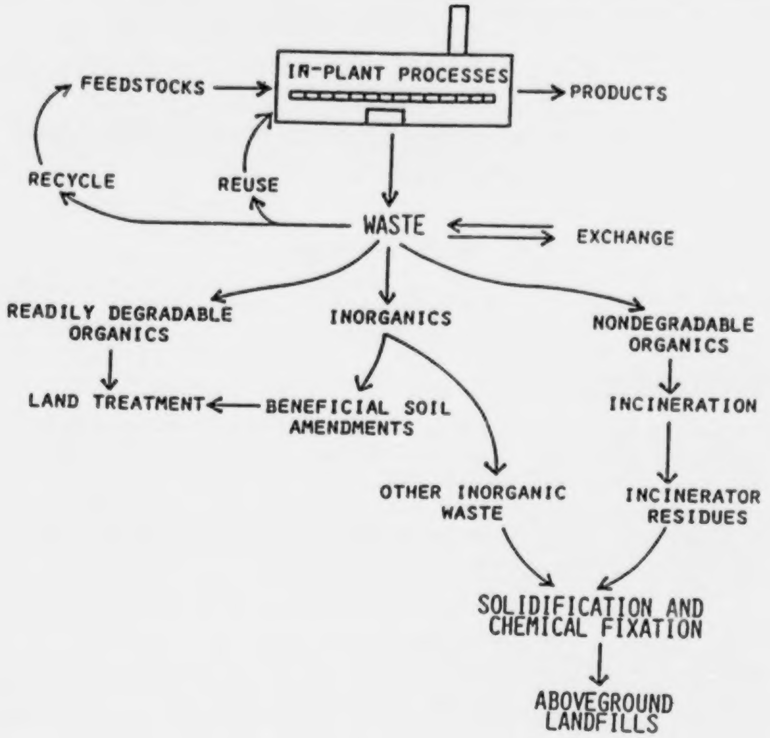
IN-PLANT PROCESSES
FEEDSTOCKS
PRODUCTS
RECYCLE
REUSE
WASTE
EXCHANGE
READILY DEGRADABLE ORGANICS
INORGANICS
NONDEGRADABLE ORGANICS
LAND TREATMENT
BENEFICIAL SOIL AMENDMENTS
INCINERATION
OTHER INORGANIC WASTE
INCINERATOR RESIDUES
SOLIDIFICATION AND CHEMICAL FIXATION
ABOVEGROUND LANDFILLS

FIGURE 1. Idealized path of hazardous waste from initial generation through final disposal.

Well documented, well run land treatment (LT) units may make the demonstration with considerably less effort. In any case, one must remember that the LTD is not performed in isolation, apart from other checks and balances to assure reliable performance. Monitoring, especially of the unsaturated zone, under a permit will provide an ongoing demonstration of treatment (or possibly lack of treatment). In this vein, the LTD may be viewed as a test to predict the most probable ultimate performance of a given unit if it is managed properly. Absolute assurance that an LT unit will continue to perform is not so essential as is using the LTD results to reject those questionable LT units that clearly cannot perform to meet the requirements.

INTENT AND USE OF GUIDANCE

Before delving into the specific approach and content of the LTD guidance, a brief digression is in order. The practice of applying hazardous wastes to land encompasses an extremely diverse population of wastes, sites and unit designs. Apart from existing facilities, use of the land treatment technology may conceivably be extended to other wastes and novel designs or settings. Guidance to address all possible circumstances must therefore either (1) be so general as to do little more than answer philosophical issues and matters of policy or (2) be presented in such detail that modifications and interpretations are always needed on a case by case basis. The suggestions and criteria presented here and in the LTD document are of the latter form, owing to the widespread call for specific information. As such, the information should, as much as possible, be used as a guidepost in choosing an LTD approach and in designing and performing the demonstration. Penetrating and sensible exchanges of information between the parties in a permitting situation are therefore essential to the tailoring of LTD plans that are suited to particular circumstances. In using the guidance, one should adapt the approach to the site rather than attempt to force fit the site into the program suggested in the LTD document.

HISTORY OF THE LAND TREATMENT DEMONSTRATION

There is nothing unique about the concept of a treatment demonstration for a LT unit. The demonstration is comparable to pilot scale testing, a widespread approach to ensure the successful operation of a production unit or process prior to full scale implementation. In the waste management area, the best parallel is perhaps the test burn requirement for incinerators. Since significant costs and environmental effects may depend upon successful land treatment performance, the EPA views the LTD as an essential step to permitting a unit. In fact, very early in the development of permitting and performance standards for LT units, the EPA adopted the concept of an LTD.

Early attempts at demonstrating treatment were, not surprisingly, adopted from land treatment research methods. Significant research on hazardous waste land treatment began in the mid-1970's and entailed a broad array of nonstandardized laboratory and field test procedures. Since an understanding was sought of the mechanisms of waste fate and behavior in soils, lab studies were emphasized that compared the relative influences of soil, waste, management, and other environmental parameters on waste treatability. Indeed, in 1984 EPA produced a draft LTD guidance document that was styled after these research efforts. An array of approximately 15 laboratory and field test systems was suggested. Complexity and cost and the reliability of extrapolating from the bench scale to the field relegated this early draft guidance to research and/or LT feasibility investigations for untested waste streams.

On the other hand, the methods suggested in the present guidance (1) in particular barrel lysimeter and field plot studies, are founded on extensive applied research and testing experience. More will be said later about the specifics of these test methods. Historically, field plot testing has been practiced in this country since the 1860's, beginning with the Morrow Plots at the University of Illinois. Numerous treatises have been written on the subject of how to design and conduct such studies. Although they have a shorter and less colorful history, lysimeters (large undisturbed soil monoliths or cores) have been employed in waste-related testing and research for fifteen years or more, including EPA and industry sponsored investigations.

APPROACH TO THE LTD

A basic tenet in preparing practical guidance for treatment demonstrations is that the most information be gathered for the least effort and cost. A second criteria is that any suggested method should be capable of being performed by anyone that has a sound applied science background. Little or no highly specialized or costly equipment should be employed, and that equipment which is used should be easily available to the facility owner/operator. Finally, the method chosen should produce data that are a fair representation of reality and which may be easily interpreted and reliably extrapolated to the full scale LT unit.

Based on the above guidelines for choosing test methods, a wide array of candidate methods were reviewed for inclusion in the LTD protocol, and many were discarded as being impractical for various reasons. Soil respirometry, batch adsorption, column leaching, and other such techniques used in research were deemed too cumbersome to be justified by the limited amount of usable information that would be obtained. Results from using these methods have not been well documented as being indicative of field performance. Instead, such methods are better applied in the research setting, rather than attempting to extrapolate their findings to the field. Two feasible basic technical approaches were identified: intensive evaluation of an existing site or extended field scale testing.

Data from an Existing Site

No better representation of the performance of an existing site may be obtained than using data from the site itself. Provided that past practices can be documented and future plans do not include major alterations in the unit (Table 1), waste quality and application rates and soils data at an existing site can provide a fair representation of the unit performance. Unless an extremely rapid downward flux of soil moisture occurs at a given site, a relatively deep, one time soil sampling and analysis program will produce a composite snapshot of the degradation and mobility of waste constituents over the life of the unit. Thus, a general mass balance of constituents may be constructed from the waste and soil data.

This mass balance should indicate that at least 70 to 80% (2) of the applied hazardous organic constituents are no longer present (i.e., apparently degraded, transformed, or immobilized) and that the concentration of each of these constituents in the zone of waste incorporation is no greater than two times the concentration (mg/kg) applied annually (3). In addition, the soil samples obtained

TABLE 1. Planned operations information needs.

Category	Conformation of No Design and Operation Changes
Unit Processes	No anticipated measurable quantities of additional hazardous or pertinent nonhazardous constituents that are not presently in the land treated wastes.
Waste Application Rates	No greater than a 20% increase in the quantities of hazardous or pertinent nonhazardous constituents applied per unit area per unit time (kg/ha/yr).
Soil	No expansion onto new soil series; no importation of different soils for use as the treatment medium; no major disruption of existing soils.

from below the treatment zone should confirm no significant leaching losses of hazardous constituents. Assuming that the unit is acceptable in these regards, then the information so obtained may suffice as a demonstration of treatment. Where such a technical approach is not feasible, or where results do not indicate adequate performance, an alternative extended study approach will be necessary.

Extended Studies

LT units that are new or those existing sites that lack sufficient records, need redesign, or are performing poorly may be required to perform extended treatment demonstration studies. The guidance identifies two appropriate test methods to achieve the desired demonstration. The applicant may use either of the two, a combination, or other justifiable methods. The suggested choices are "barrel" lysimeter or field plot studies.

Barrel Lysimeters. A close approximation to field conditions may be achieved by using a large undisturbed soil column instrumented and enclosed within some watertight container. The term "lysimeter" is applied to such a device, consistent with soils nomenclature but not to be confused with the regulatory term for any soil-pore liquid sampling device. Sufficient dimensions to encompass many of the macroscale soil features will effectively overcome most of the shortcomings of soil microcosm tests. On the other hand, the control that may be exerted on the barrel size column is superior to that which can be achieved on the field plot scale. Associated costs should also fall below those for field plots.

Mindful of the intent stated previously of using easily obtainable, relatively nonspecialized equipment, the barrel configuration was chosen. Since it consists of no more than an open-ended, nonribbed 55 gallon drum, the barrel is inexpensive, easily obtainable, and easily installed and instrumented (Figure 2). Once the soil core is collected, the barrel is fitted with a leachate collection system and the bottom is sealed. The lysimeter is installed partially or completely below grade in an isolated, sheltered area or even below the surface of the LT unit (depending on the experimental design). The experimental design (i.e., number of wastes, waste loading rates, and number of replications) also will prescribe the number of barrels needed.

All essential aspects of the treatment demonstration may be monitored and interpreted using the barrel lysimeter. Controlled waste applications may be carefully measured, soil sampling can be used to characterize organics degradation, and soil cores and leachate collection can be used to assess the potential for vertical migration of waste constituents. The relatively large core size enables realistic simulation of management methods. Since future regulatory requirements also include monitoring air emissions, the barrels may easily be fitted with air sampling chambers, some of which have already been developed for the barrel configuration.

Field Plots. The closest approximation to full-scale field operations that retains a reasonable degree of experimental control involves the use of field plots. Basically, plots consist of small tracts of land that are designed or located so as to separate them from ongoing land treatment operations. These plots are instrumented with soil-pore liquid sampling devices, and bermed, sloped, and managed to closely reproduce full-scale operations (Figure 3). For a relatively well operated LT unit, plots may be established on the active unit. In practice, plot sizes are dependent upon a number of considerations, including: (a) Experimental design; (b) Equipment used in the full scale operation; (c) Size of the entire LT unit; (d) Performance as indicated by reconnaissance data for existing units; and (e) Cost.

While the field plots most nearly represent the actual operational conditions, environmental factors can hinder acquisition of acceptable results. No control is possible, for example, on the amount and temporal distribution of precipitation, apart from installation of automated rain shelters. Therefore, should an LTD study be performed during an unseasonably dry year, the investigator and the reviewer may question the possible influence that a wetter year might have had on hazardous constituents degradation and mobility. Longer term testing requirements than in the barrel lysimeter studies may be needed.

Extended Study Interpretations. Regardless of which extended study method is used, the interpretations must attempt to extrapolate relatively short term findings into a projection of long term unit performance. Special concerns in such an extrapolation include the unknown effects of repeated waste applications, the potential buildup of toxic constituents, and the effects of extremely wet years on hazardous constituent leaching. However, to repeat an earlier statement, the LTD

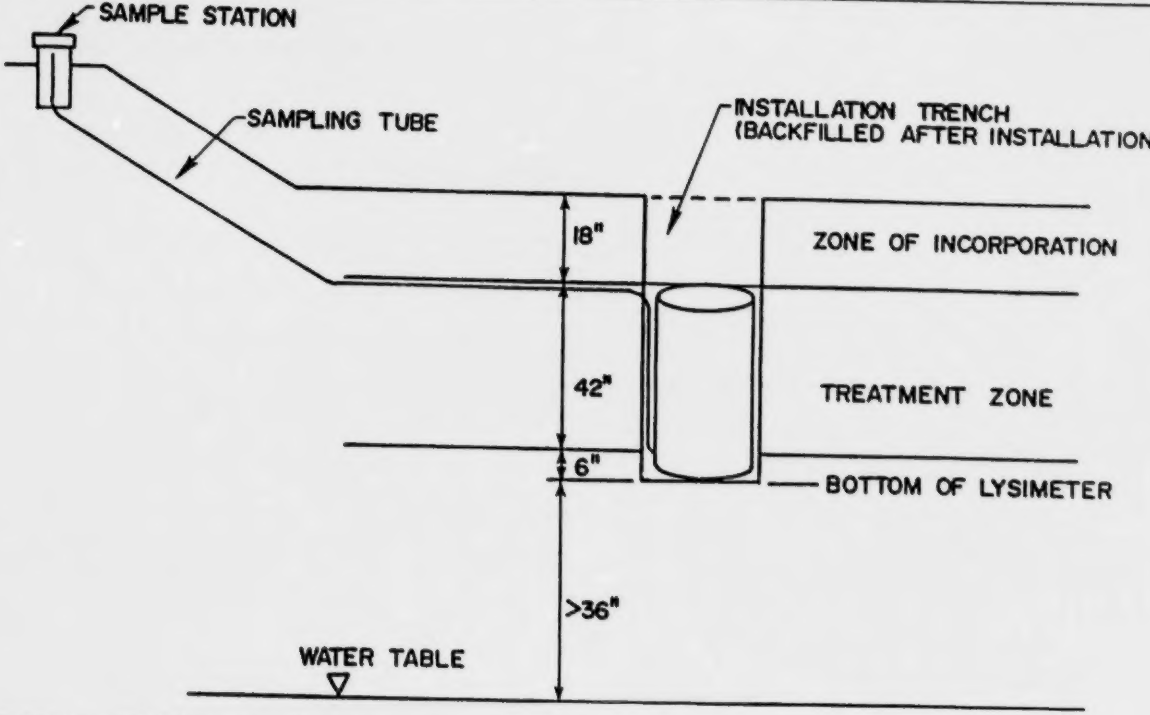
SAMPLE STATION
SAMPLING TUBE
INSTALLATION TRENCH
(BACKFILLED AFTER INSTALLATION)
18"
ZONE OF INCORPORATION
42"
TREATMENT ZONE
6"
BOTTOM OF LYSIMETER
>36"
WATER TABLE

FIGURE 2. Installation of barrel lysimeter.

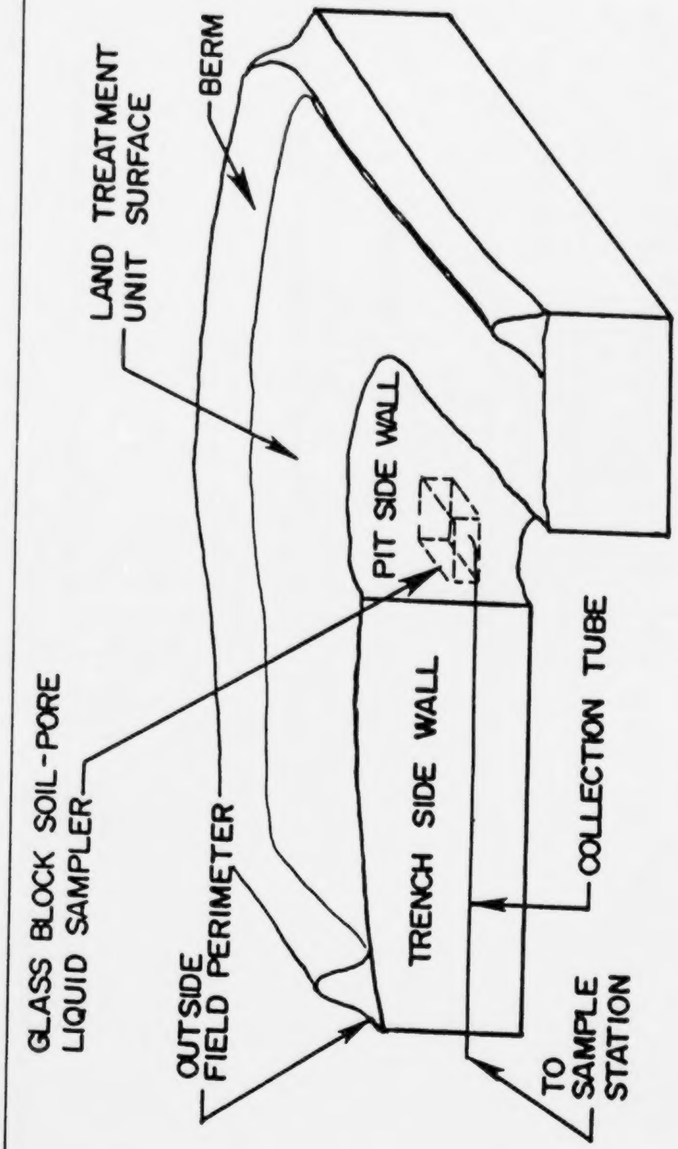
GLASS BLOCK SOIL-PORE LIQUID SAMPLER
OUTSIDE FIELD PERIMETER
LAND TREATMENT UNIT SURFACE
BERM
PIT SIDE WALL
TRENCH SIDE WALL
COLLECTION TUBE
TO SAMPLE STATION

FIGURE 3. Generalized field plot design.

may be viewed as a test to predict the most probable ultimate performance of a given unit. As such, the interpreter must recognize that the facility will receive continued monitoring to confirm continued performance and support continued operation.

Equipped with this perspective, the interpreter should express LTD results in terms of acceptable annual waste loading rates based on half-lives of hazardous organic constituents or gross organic fractions. At this time, there are no proven techniques for calculating these acceptable annual waste loading rates, but the guidance manual suggests a toxicity based approach that limits waste buildup in soil to the threshold concentrations that induce microbial toxicity. Apart from calculating waste loading rates using toxicity information, only one other approach appears feasible. That approach relates waste organics buildup in soil to the time that will be needed to close the site, accounting for degradation rates and final target soil concentrations for the constituents of concern. In some cases, the LTD may reveal that no hazardous organic constituent remains in the soil in a detectable concentration. Loading rates would thus be controlled by other factors, such as hydraulic loading.

In addition, the interpretation should confirm that no significant migration of hazardous constituents will occur below the treatment zone. Mobility results will ordinarily consist of soil-pore liquid and soil core analytical data, and statistical comparisons are made with background conditions. Leaching potential may, in some cases, be the controlling factor in establishing waste loading rates rather than degradation information. Likewise, if volatilization is considered, some situations may warrant limitations on loading rates based on air emissions.

CONCLUSIONS

The LTD is a tool for predicting probable LT unit performance, and the results form the basis for a large number of permit conditions, such as waste application rates and methods, and constituents to be analyzed for the monitoring program. Where conditions warrant, the best approach makes use of existing data in tailoring the LTD method to the specific circumstance. Extended studies, if needed, should emphasize reliable representation of field conditions. Thus, large scale soil macrocosm testing or field plot studies may be necessary. In any case, the ability to interpret results and make reasonable recommendations which will aid in practical, environmentally sound methods for day to day management of the LT unit is of primary importance in designing and carrying out the LTD.

REFERENCES

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MODELING OF PROCESSES IN THE UNSATURATED ZONE

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Land treatment has been practiced by the petroleum refining industry for over twenty years with a great deal of success. This practice has led to the development of procedures and operation guidance that, by and large, permit the environmentally acceptable operation of these facilities. However, industries other than petroleum refining are using, or are considering the use of land treatment. Expanding the application of this technology in an orderly and environmentally acceptable manner will require an understanding of the various processes that occur in the treatment zone as well as the interactions of each process. One tool that could be useful to the understanding and application of land treatment technology is mathematical modeling of the treatment zone by application of the transport equations. To date, little effort has been made toward mathematical modeling of land treatment.

The objective of this paper is to point out ways that the models can be utilized to aid in land treatment evaluation, regulation, design, and research. Mathematical models can be used to evaluate laboratory screening data to help determine whether or not a specified waste can be treated at any given location. Also, these models can be used to determine what are the principle hazardous constituents (PHCs) in a given waste. The principle hazardous constituents are the components of the waste that are most mobile and relatively persistent in the unsaturated zone. As such, they are the ones which should be most closely monitored. Models can also be used to estimate the amount of volatile materials that will escape into the atmosphere from a land treatment plot. At this point, let us examine the transport equations and their development.

TRANSPORT EQUATIONS

The development of the transport equation begins with a material balance around a differential element as shown in Figure 1. It is first envisioned that water is flowing through the soil at a constant velocity, V_a. The water carries with it a dissolved component of interest which has a concentration, C_a. This component can be sorbed by the soil or degraded by the soil microbes. Thus, the con-

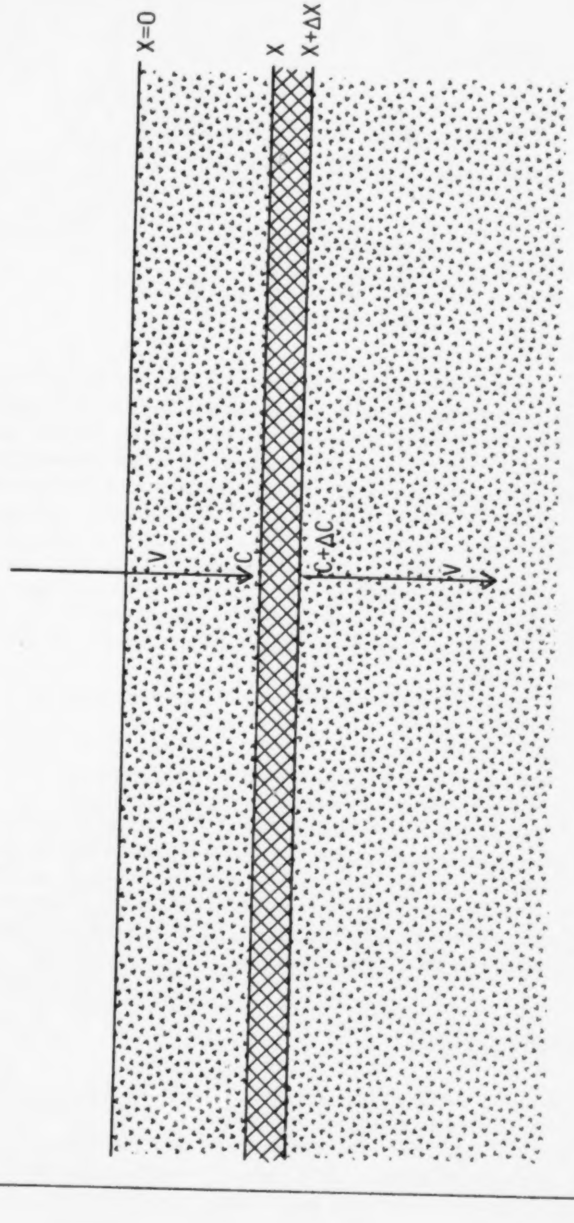
X=0
X
X+ΔX
V
C
C+ΔC
V

FIGURE 1. Material balance for transport equation.

centration of the component will be a function of both depth and time. A differential material balance yields:

$$\frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial X^2} - V_a \frac{\partial C_a}{\partial X} - \frac{\rho}{\theta}\frac{\partial C_s}{\partial t} - \mu_a C^a - (\rho/\theta)\,\mu_s C_s \qquad (1)$$

Where t is time, D is the dispersion coefficient, X is the depth, ρ is the bulk density of the soil, θ is the volumetric water content of the soil, C_s is the concentration of the pollutant in the soil phase (weight of component per unit weight of soil), μ_a is the first-order degradation constant in the aqueous phase, μ_s is the first-order constant in the soil phase, and K_D is the sorption constant. Equation (1) assumes that the sorption of the component of interest by the soil can be expressed in terms of a linear isotherm as shown in the following:

$$C_s = K_D C_a \qquad (2)$$

Equation (1) can be rearranged as shown below:

$$\left[1 + \frac{\rho K_D}{\theta}\right] \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial X^2} - V_a \frac{\partial C_a}{\partial X} - \mu_a C_a - \frac{\rho \mu_s K_D C_a}{\theta} \qquad (3)$$

By defining a retardation factor and a new degradation coefficient as:

$$R = 1 + \rho\,(K_D/\theta) \qquad (4)$$

$$\mu = \mu_a + \mu_s\,(\rho K_D/\theta) \qquad (5)$$

The transport equation thus becomes:

$$\frac{\partial C_a}{\partial t} = \frac{D_a}{R}\left(\frac{\partial^2 C_a}{\partial X^2}\right) - \frac{V_a}{R}\left(\frac{\partial C_a}{\partial X}\right) - \frac{\mu C_a}{R} \qquad (6)$$

PLUG FLOW WITH NO DEGRADATION

In order to visualize the effect of the various parameters in the transport equation we will examine the solution of equation (6) for the case where dispersion and the transformation rate is assumed to be zero. The transport equation simplifies to the following:

$$R \frac{\partial C_a}{\partial t} = -V_a \frac{\partial C_a}{\partial X} \qquad (7)$$

For the case where a step input of pollutant is applied to the soil, the following boundary conditions can be used:

BC:

$$C_a = 0 \qquad \text{for all } X > 0 \text{ at } t = 0 \tag{8}$$

$$C_a = C_i \qquad \text{for all } t > 0 \text{ at } X = 0 \tag{9}$$

$$C_a \to 0 \qquad \text{as } X \to \infty \tag{10}$$

The solution to equation (7) with the boundary conditions (8), (9), and (10) is:

$$C_a/C_i = S \begin{cases} S = 1 \text{ for } X \le V_a t/R \\ S = 0 \text{ for } X > V_a t/R \end{cases} \tag{11}$$

Figure 2 shows a graphical representation of this solution. The relative concentration profile is such that at any given point, the relative concentration is either 0 or 1 depending on whether or not "break-through" has occurred. The pollutant moves through the soil with a very sharp profile because of the assumed lack of dispersion. The velocity with which the pollutant moves is determined by the interstitial velocity of the water and the retardation factor as shown below:

$$V_p = V_a/R \tag{12}$$

Where V_p is the pollutant velocity. Equation (7) can also be solved for a pulse input. For this case, the following boundary conditions apply.

BC:

$$C_a = 0 \qquad \text{for all } X > 0 \text{ at } t = 0 \tag{13}$$

$$C_a = C_i \qquad \text{for all } t \ge 0 \text{ and } t \le L/V_p \text{ at } X = 0 \tag{14}$$

$$C_a = 0 \qquad \text{for } t > L/V_p \text{ at } X = 0 \tag{15}$$

The solution to equation (7) with the boundary conditions (13), (14), and (15) is:

$$C_a/C_i = P \begin{cases} P = 0,\ X \le V_a t/R - L \\ P = 1,\ V_a t/R - L \le X \le V_a t/R \\ P = 0,\ X > V_a t/R \end{cases} \tag{16}$$

where L is the length of the pulse. This solution is graphically represented in Figure 3. The pollutant moves through the soil as a constant pulse with a velocity equal to V_p as defined by equation (12).

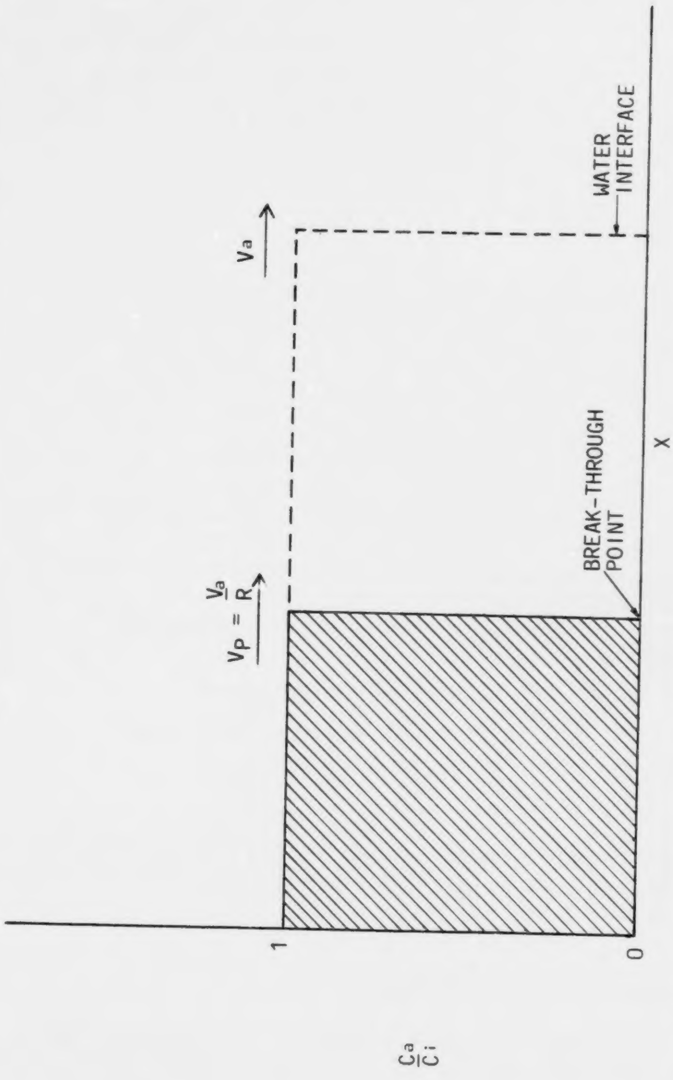

FIGURE 2. Concentration profile: step input.

PLUG FLOW WITH BIOLOGICAL DEGRADATION

For land treatment applications, biological degradation of the hazardous waste components is of utmost importance. Land treatment requires this degradation to convert hazardous organic wastes to innocuous materials. If we are to apply the transport equations to land treatment, degradation is essential. The usual assumption is that degradation in the soil proceeds according to first order kinetics. This degradation can be represented as is shown in equation (5). For plug flow the transport equation (6) reduces to:

$$R\,\frac{\partial C_a}{\partial t} = -V_a\,\frac{\partial C_a}{\partial X} \quad \mu C_a \tag{17}$$

As before, equation (17) can be solved for the case of step and pulse inputs. The solution using the appropriate boundary conditions gives the following for a step input.

$$\frac{C_a}{C_i} = Se^{-\mu x/v_a} \begin{cases} S = 1, X \leq V_a t/R \\ S = 0, X > V_a t/R \end{cases} \tag{18}$$

Figure 4 presents a graphical representation of this solution which is similar to the nondegradation case. However, as the pollutant moves through the soil, its concentration is attenuated by biological degradation to a level equal to the concentration predicted by first-order kinetics, i.e., $C = C_i e^{-\mu t}$. Likewise, equation (17) can be solved using the boundary conditions for pulse input. This yields the following solution:

$$\frac{C_a}{C_i} = Pe^{-\mu x/v_a} \begin{cases} P = 0, X \leq V_a t/R - L \\ P = 1, Vt/R - L \leq X \leq V_a t/R \\ P = 0, X > V_a t/R \end{cases}$$

Figure 5, presents a graphical representation of this solution. Again, it is similar to the nondegradation case except that the concentration is attenuated as it moves through the soil.

HYDRODYNAMIC DISPERSION

When modeling the transport of pollutants, an important consideration is hydrodynamic dispersion. By and large, when dissolved pollutants are transported through the soil they move in the direction of the bulk flow of the water (advection). However, there is a tendency for the pollutant to spread out from the flow path. This spreading dilutes the pollutant. Dispersion is a result of mechanical mixing during flow and molecular diffusion. Molecular diffusion is only important in the dispersion process at low flow velocities.

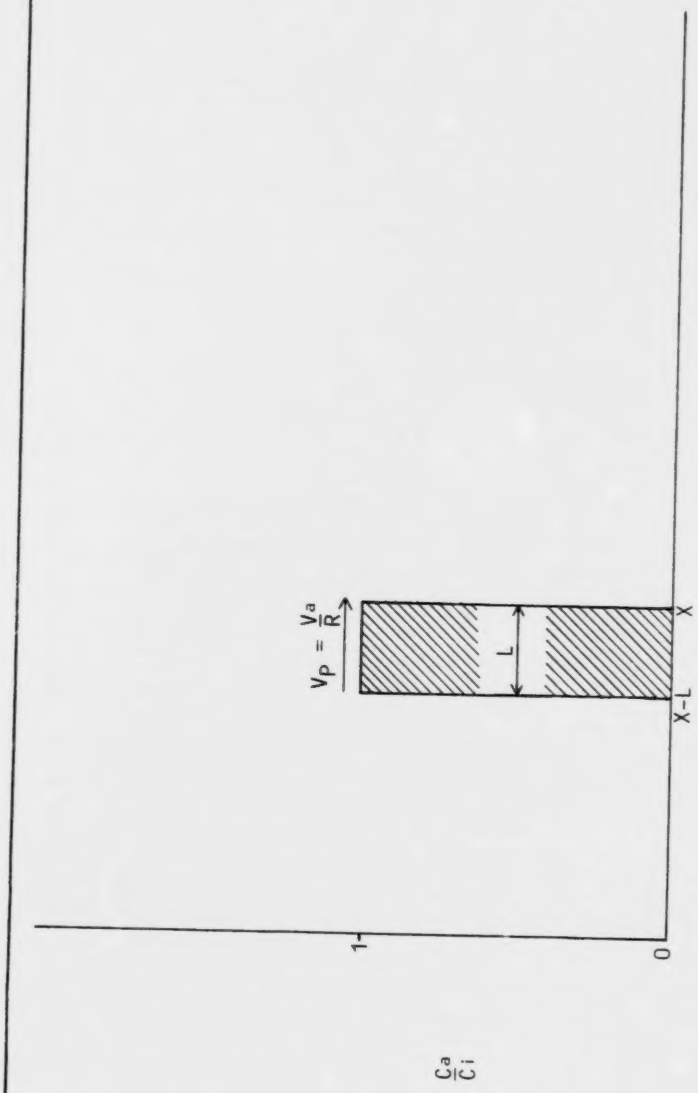
$V_P = \frac{V_a}{R}$
L
X–L
X
1
0
$\frac{C_a}{C_i}$

FIGURE 3. Concentration profile: pulse input.

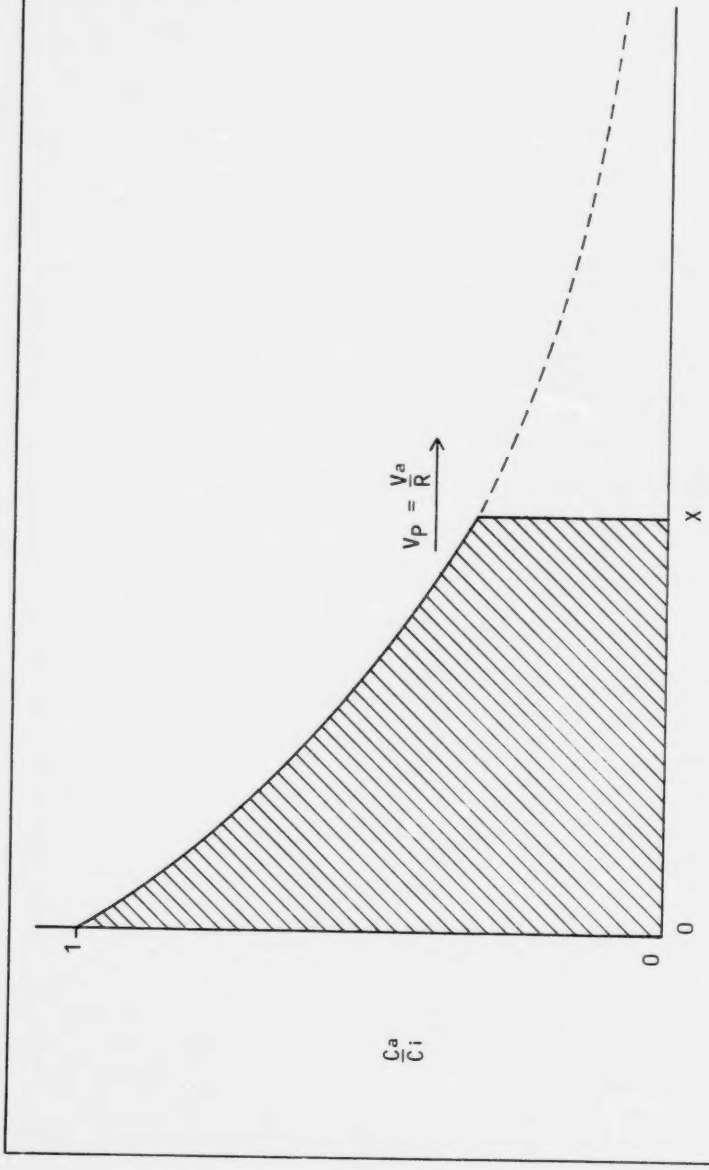

FIGURE 4. Concentration profile: step input with biodegradation.

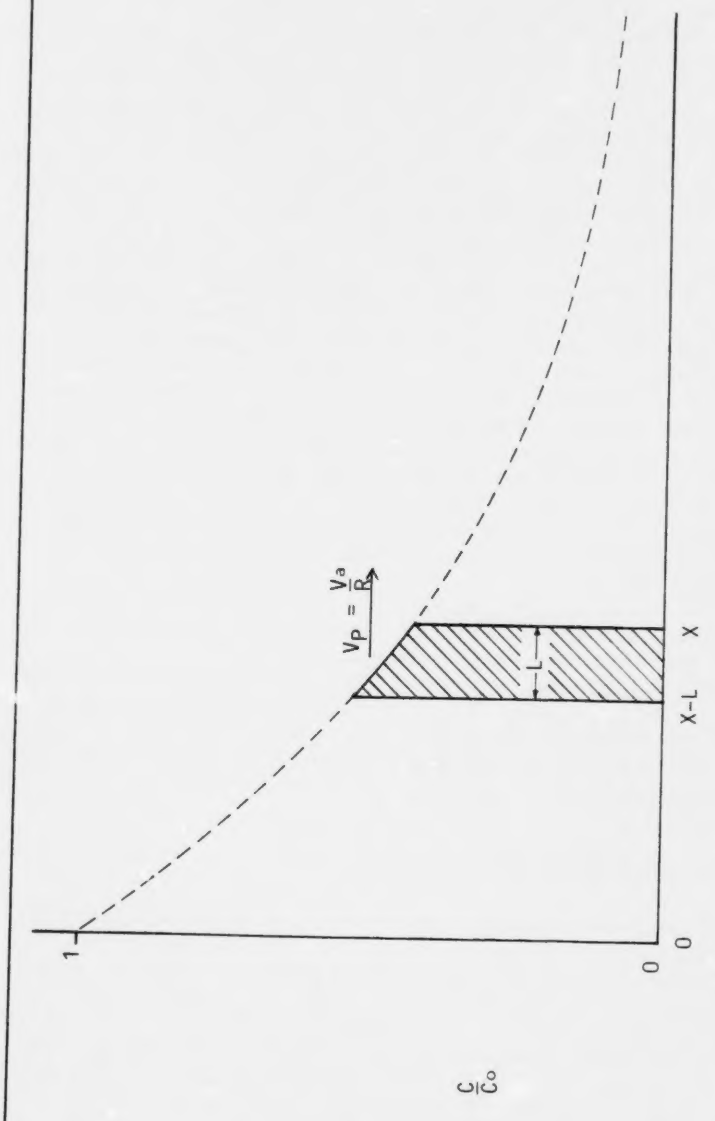

FIGURE 5. Concentration profile: pulse input with biodegradation.

The effect of hydrodynamics can be illustrated by the following example. Consider a soil column which is completely saturated with water at the beginning of an experiment. The water is allowed to move through the column at a uniform velocity. At time equal zero, a nonvolatile, nondegradable tracer is added to the feed water at a concentration equal to C_i. The response is illustrated in Figure 6. Shown is the relative concentration of the tracer that exits from the column, as a function of time. If it were not for dispersion, the tracer would move through the column in plug flow fashion and would exit at "break-through" as a step function. However, in a real situation, hydrodynamic dispersion does occur and causes "break-through" to be spread out. The tracer will first appear at the exit earlier than would be expected from the bulk flow of water. Also, the full concentration of the tracer would not be observed until later than expected.

Hydrodynamic dispersion can be caused by four mechanisms. The first mechanism is illustrated in Figure 7. The velocity within individual pores assumes different velocities at different points due to drag forces exerted on the fluid by the soil particles as the fluid moves across the surface of the particles. This variation in velocity causes some molecules of the pollutant to move faster than others. The result is a spreading in the direction of bulk flow (longitudinal dispersion).

The second mechanism is illustrated in Figure 8. Different pore sizes for each flow path of the water causes water in some pores to move faster than water in other pores. This difference in velocities contributes to longitudinal dispersion.

The third mechanism is illustrated in Figure 9. Tortuosity, branching, and interfingering of pore channels allows the fluid to travel via several paths of varying lengths and direction. The result is a spreading of the pollutant transversal to the direction of flow.

The last mechanism is illustrated in Figure 10. This mechanism is molecular diffusion which is driven by differences in concentration of the pollutant. The result is both longitudinal and transverse dispersion.

Equation (6) represents the transport equation for the case of a nonvolatile pollutant dissolved in water. This equation has been solved analytically for a wide variety of boundary conditions, e.g., see van Genuchten 1982. If an analytical solution for a desired set of boundary conditions does not exist in the literature, then a wide variety of numerical techniques are available.

MULTI-PHASE TRANSPORT EQUATION

Land treatment is a far more complex problem than a dissolved pollutant moving through the soil. Not only is soil and water present, materials being land treated normally consist of a nonsoluble oily material in which the hazardous components are dissolved. Usually, the hazardous components are highly soluble. Volatilization is possible and in some cases is very likely to occur. Possible losses of pollutants to the atmosphere must be considered. Enfield et al. (1985) and Jury et al. (1983) have considered transport equations in which a vapor phase was considered. A transport equation for land treatment can be derived which allows an oil phase as well as volatilization.

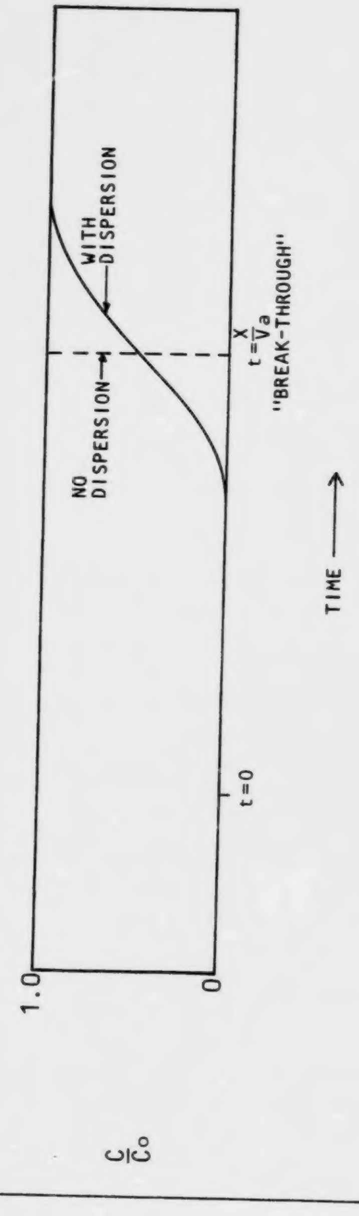

FIGURE 6. Response of soil column to step input of tracer.

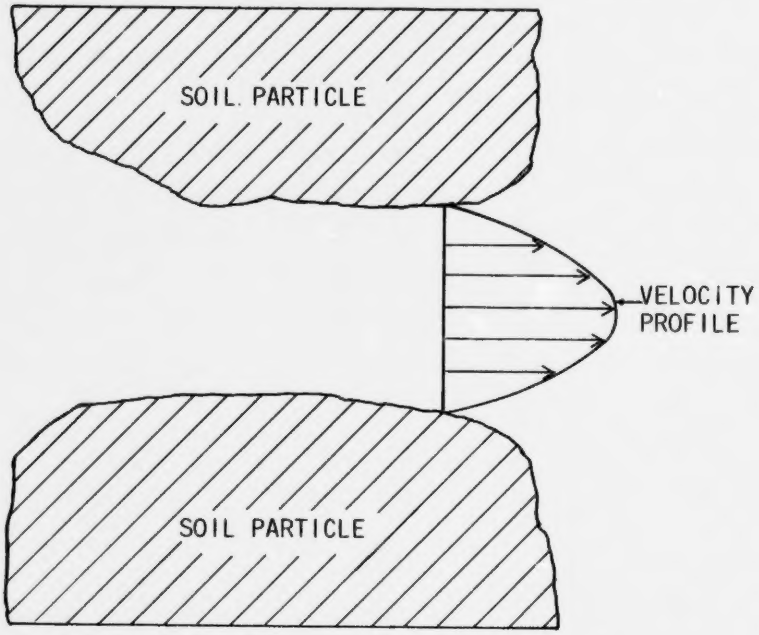

FIGURE 7. Dispersion by velocity profile within individual pores.

Consider the transport of pollutants through aqueous, soil, vapor, and immiscible oil phases. A differential material balance is written for each phase assuming local equilibrium and first-order degradation kinetics. Note that since local equilibrium is assumed, the net interphase transport is zero. For example, the rate of mass transfer of the pollutant from the aqueous phase to the solid phase is exactly equal to the rate of mass transfer from the solid phase to the aqueous phase. Also, the assumption is made that the relative amounts of each phase (aqueous, soil, vapor, and oil) remains constant through the soil profile.

Aqueous phase - $$\theta(\partial C_a/\partial t) = \theta D_a \frac{\partial^2 C_a}{\partial x^2} - \theta V_a \frac{\partial C_a}{\partial x} - \mu_a \theta C_a \qquad (19)$$

where: θ = volumetric water content (M^3/M^3); C_a = concentration of the pollutant in the aqueous phase (gm/M^3); X = distance below the surface (M); D_a = dispersivity coefficient of the pollutant in the aqueous (M^2/D); V_a = interstitial velocity of the aqueous phase (M/D); $\mu_a 0$ = first-order rate constant for degradation in the aqueous phase (1/D)

Soil phase -
$$\rho\ (\partial C_s/\partial t) = -\mu_s \rho C_s \tag{20}$$

where: ρ = density of the soil phase (gm/M^3); C_s = concentration of the pollutant in the soil phase (g/Kgm); μ_s = first-order rate constant for degradation in the soil phase (1/D)

Immiscible Oil Phase -
$$\phi\ (\partial C_o/\partial t) = D_o \phi \frac{\partial^2 C_o}{\partial x^2} - V_o \phi \frac{\partial C_o}{\partial x} - \mu_o \phi C_o \tag{21}$$

where: ϕ = volumetric oil content (M^3/M^3); C_o = concentration of the pollutant in the oil phase (gm/M^3); D_o = dispersivity coefficient of the pollutant in the oil phase (M^2/D); V_o = interstitial velocity of the oil phase (M/D); μ_o = first-order rate constant for degradation in the oil phase (1/D)

Vapor Phase -
$$\eta\ (\partial C_v/\partial t) = D_v \eta \frac{\partial^2 C_v}{\partial x^2} - V_v \eta \frac{\partial C_v}{\partial x} - \eta \mu_v C_v \tag{22}$$

where: η = volumetric vapor content (M^3/M^3); C_v = concentration of the pollutant in the vapor phase (gm/M^3); D_v = dispersivity coefficient of the vapor phase pollutant (M^2/D); V_v = interstitial of the vapor phase (M/D); μ_v = first-order rate constant for degradation in the vapor phase (1/D).

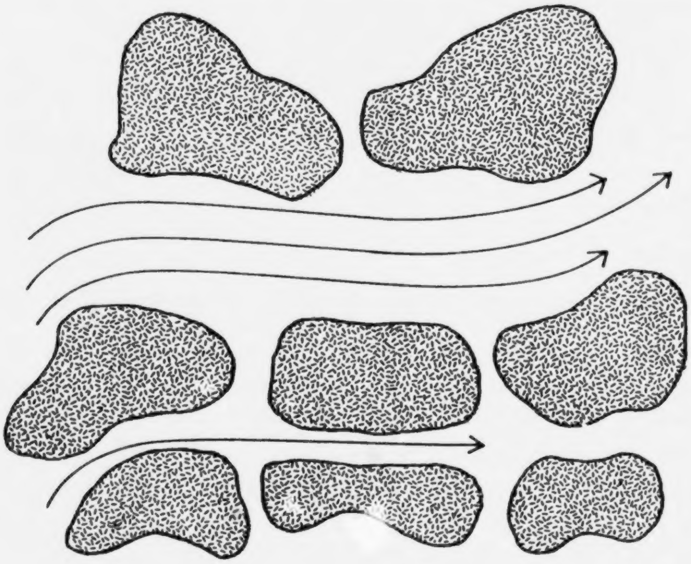

FIGURE 8. Dispersion by variations in pore size along flow path.

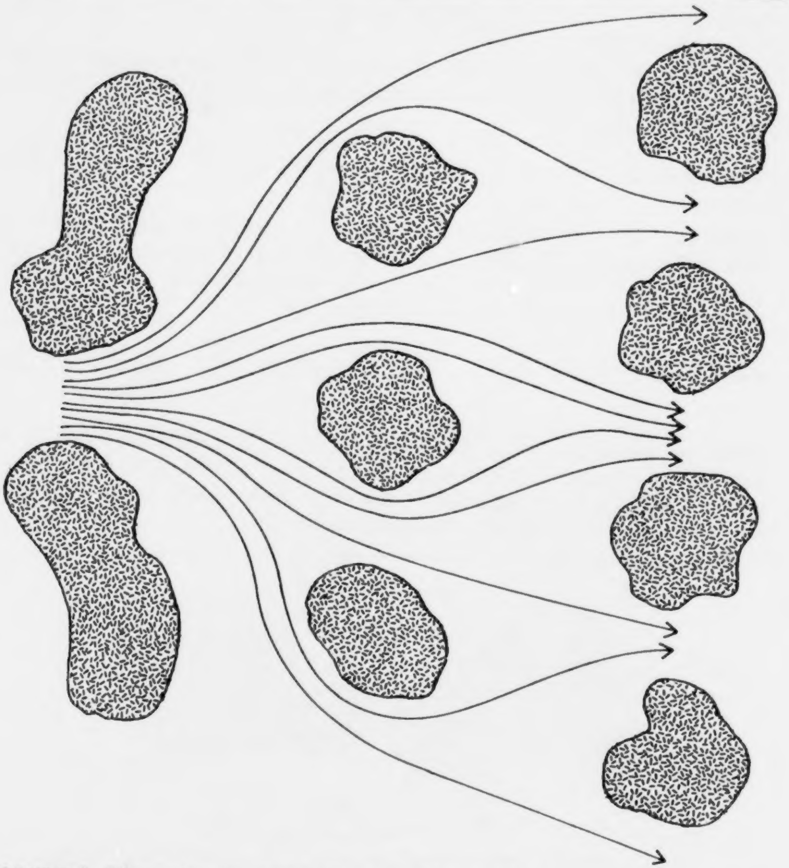

FIGURE 9. Dispersion by tortuosity, branching, and interconnecting of pore channels.

Equations (19), (20), (21), and (22) can be combined to give an expression for the transport through out the entire system.

$$\begin{aligned}\theta\frac{\partial C_a}{\partial t}+\phi\frac{\partial C_o}{\partial t}+\eta\frac{\partial C_v}{\partial t}+\rho\frac{\partial C_s}{\partial t} &= D_a\theta\frac{\partial^2 C_a}{\partial x^2}+D_o\phi\frac{\partial^2 C_o}{\partial x^2}+D_v\eta\frac{\partial^2 C_v}{\partial x^2}\\ &\quad - V_a\theta\frac{\partial C_a}{\partial x} - V_o\phi\frac{\partial C_o}{\partial x} - V_v\frac{\partial C_v}{\partial x}\\ &\quad - \mu_a\theta C_a - \mu_o\phi C_o - \mu_v\eta C_v - \mu_s\rho C_s \qquad (23)\end{aligned}$$

The total concentration of the pollutant can be expressed as a sum of the concentrations in each phase.

$$C_T = \theta C_a + \phi C_o + \eta C_v + \rho C_s \tag{24}$$

To describe the partitioning of the pollutant between the soil and the aqueous phase, we assume a linear isotherm. This yields a simple linear relationship for solid-liquid partitioning.

$$C_s = K_D C_a \tag{25}$$

Partitioning of the pollutant between the aqueous and vapor phases is represented by Henry's Law.

$$C_v = K_H C_a \tag{26}$$

In order to describe the partitioning of the pollutant between the soil and aqueous phases, we use a simple linear partitioning relationship.

$$C_o = K_L C_a \tag{27}$$

Under the assumption of local equilibrium, equations (25), (26), and (27) are sufficient to completely describe the distribution of the pollutant among the aqueous, oil, vapor, and solid phases. Using equation (24) and these linear relationships, we can write an expression for the total concentration in terms of the individual phase concentrations.

$$C_T = B_a C_a = B_o C_o = B_v C_v = B_s C_s \tag{28}$$

where:

$$B_a = [\theta + \phi K_L + \eta K_H + \rho K_D] \tag{29}$$

$$B_o = [(\theta/K_L) + \phi + \eta(K_H/K_L) + (\rho K_D/K_L)] \tag{30}$$

$$B_v = [(\theta/K_H) + \phi(K_L/K_H) + \eta + (\rho K_D/K_H)] \tag{31}$$

$$B_s = [(\theta/K_D) + \phi(K_L/K_D) + \eta(K_H/K_D) + \rho] \tag{32}$$

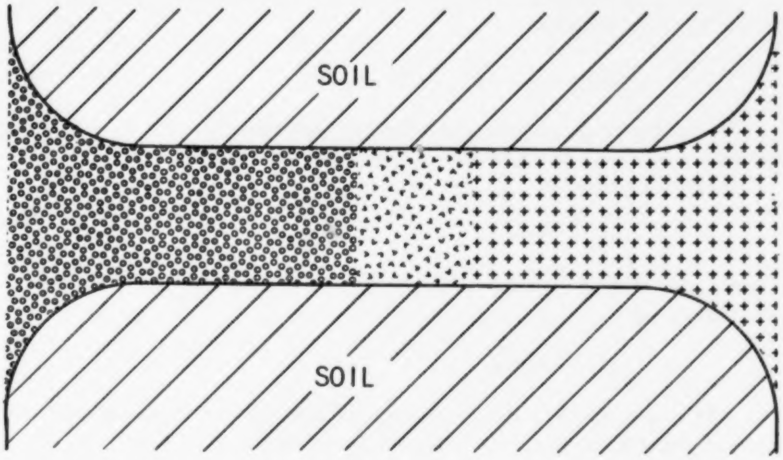

FIGURE 10. Dispersion by molecular diffusion.

Now equation (27) can be rewritten as

$$(\partial C_T/\partial t) = D_E(\partial^2 C_T/\partial X^2) - V_E(\partial C_T/\partial X) - \mu_E C_T \quad (33)$$

Where D_E, V_E, and μ_E are the effective dispersion coefficient, effective velocity, and degradation rate constant, respectively, as defined by

$$D_E = (D_a\theta/B_a) + (D_o\phi/B_o) + (D_v\eta/B_v) \quad (34)$$

$$V_E = (V_a\theta/B_a) + (V_o\phi/B_o) + (V_v\eta/B_v) \quad (35)$$

$$\mu_E = (\mu_a\theta/B_a) + (\mu_o\phi/B_o) + (\mu_v\eta/B_v) + (\mu_s\rho/B_s) \quad (36)$$

Equation (33) is the transport equation which describes the movement of a pollutant through a soil, aqueous, oil, and vapor system. Note that this equation has exactly the same form as the original transport equation. The only difference is the dispersion coefficient, velocity, and degradation rate constants are redefined as effective values. If desired, equation (33) could be transformed to express the concentration in any one of the phases rather than the total concentration by applying equation (28).

APPLICATION OF THE TRANSPORT EQUATION TO LAND TREATMENT

Laboratory Screening

"Resource Conservation Recovery Act (RCRA)" regulations require a treatability demonstration before a land treatment permit can be issued. The treatment demonstration can be accomplished using published literature data, laboratory tests, or field-scale studies. A laboratory screening protocol has been recently proposed by Matthews and Short (1984). This protocol calls for a number of tests which include studies on waste characterization, soil characterization, microbial degradation, toxicity, immobilization, and volatilization. It was envisioned that this protocol would be most useful in trying to determine whether or not there would be a significant environmental risk from the land treatment of a hazardous waste in a higher-level, field-scale treatability demonstration.

In an effort to standardize the evaluation of the data from the protocol, a rating scheme was proposed. Waste/soil mixtures were to be assigned a numerical rating which would reflect the land treatability potential. A rating of 0 to 50 represents a high potential. Ratings greater than 50 represent a low potential. The final numerical rating is derived by first establishing a baseline rating based on degradation kinetics, mobility characteristics, and potential leachable concentrations of the principal organic hazardous constituents identified in the waste. Ratings for negative factors associated with the three major areas of concern (degradation/transformation, immobilization/transport, and toxicity) are then added to this baseline rating to insure that all potential problem areas are adequately addressed.

The rating system for the negative factors is somewhat subjective. Its use must be tempered with good judgment. The baseline numerical rating is derived from the transport equations. The method for developing the rating is based on a concept put forth by Rao (1983). The concept states that the land treatability of a hazardous component is related to the depth that the components penetrate the treatment zone. The farther the penetration, the less land-treatable is the component. To develop the baseline rating, we evaluate the steady-state case of the input of a component at constant input concentration to the soil, ignoring the effects of dispersion. Under these assumptions, equation (18) will apply and can be expressed as:

$$C_a/C_i = \mathrm{EXP}(-\mu x/V_a) \tag{37}$$

Also, assume that the degradation rate in the aqueous phase μ_a equals the degradation rate in the soil phase μ_s. Use equations (4) and (5) to evaluate the first-order reaction rate constant

$$\mu = \mu R \tag{38}$$

Therefore

$$(\mu RX/V_a) = 1n(C_a/C_i) \tag{39}$$

Land treatment is successful if no detectable concentration of the hazardous component can be found below the treatment zone. Thus, we express the depth of penetration in terms of the detectable concentration of the pollutant.

$$X = (V/\mu R) \ln (C_i/C_{DL}) \qquad (40)$$

Where C_{DL} is the analytical detection limit for the pollutant. For convenience, the first-order degradation rate constant is expressed in terms of the "half-life" by:

$$t_{1/2} = (0.693/\mu) \qquad (41)$$

A base numerical rating (B.N.R.) is defined in terms of the depth of penetration (X) such that when X equals the depth of the treatment zone (Z), the B.N.R. equals 100. Therefore:

$$\text{B.N.R.} = [X(100)]/Z \qquad (42)$$

Substituting equations (45) and (46) into (45) yields:

$$\text{B.N.R.} = [(144.3)V_a t_{1/2}/RZ] \ln (C_i/C_{DL}) \qquad (43)$$

In order to apply equation (43), the interstitial velocity of the water, the half-life of the pollutant, the retardation factor of the pollutant, the depth of the treatment zone, the initial concentration of the pollutant in the aqueous phase, and the analytical detection limits of the pollutant expressed as a concentration in the aqueous phase must be known.

The interstitial velocity can be derived from historical rainfall records combined with information on the site regarding soil type, slope of the plots, and type of vegetation cover (if any). The half-life of the pollutant must be developed from either degradation experiments or literature references. The retardation factor can be derived from isotherm tests or appropriate literature data adjusted to the soil at the site of interest. The depth of the treatment zone is normally 1.5 meters (adjusted according to regulations for cases where the water table is close to the surface). The input concentration must be developed using leaching tests on the actual waste.

The assumption of no dispersion and constant input of the pollutant while, totally correct, does give results that are "conservative." That is, equation (47) will give a rating that is higher (less land treatable) than would be the case if calculations were made by not making these assumptions.

Principal Hazardous Constituents

Land treatment, in order to be environmentally acceptable, must be properly managed to assure that there is no adverse impact upon groundwater by the operation of the facility. Hazardous compounds must not escape the treatment zone. They must be retained within the treatment zone until they can be thoroughly degraded, transformed, or immobilized. An unsaturated zone monitoring program to sample the soil and pore water is essential to the management of the treatment facility. In addition, a monitoring program will be specified as part of the land treatment permit. Section 264.278(a) of the Federal Register (Vol. 47, No. 143, Pg. 32329, July 26, 1982) allows the regional administrator to specify certain "Principal Hazardous Constituents" (PHCs) for monitoring purposes. The purpose of specifying PHCs is to reduce the burden on certain land treatment operators to monitor all hazardous components without compromising the environment. The operator can monitor for these constituents instead of all waste constituents. The detection of these PHCs below the treatment zone would serve as an early warning that treatment at the facility was failing. Thus, the regulations specify that the PHCs should be the least degradable, most mobile, and be present in high enough concentrations to detect. One concern of a permit writer will be the potential for the selection of PHCs. Rao (1983) has proposed a selection criteria for PHCs and is currently working under a cooperative agreement (CR811035) with EPA to develop a protocol for PHCs selection. His selection method is based upon a simulation model using the transport equations. Using the transport equations, he derived the following equation for plug flow of a continuous application of a waste constituent at steady state.

$$1n\,(C_i/C_o) = -(\mu R)\,[(X/V_a)] \tag{44}$$

where: C_o is the concentration at depth X; C_i is the applied concentration; and X is the depth.

Thus, he concluded that for land treatment, the product μR designated as β is a characteristic for each waste component. Note that β takes into account retardation of leaching and attenuation due to degradation. It is obvious that the smaller the coefficient, the more likely a component is to arrive at the bottom of the treatment zone at sufficient concentrations. Hence, a ranking of waste constituents on the basis of β should be useful in selecting PHCs for a specific waste stream designated for a specific land treatment site.

VOLATILE EMISSIONS

Volatile emissions from land treatment and land disposal sites have received little attention until recently. Data collected from ambient air measurements of the Love Canal and from the Hudson River Basin indicate that significant concentration of toxic materials can be released, often much greater emissions via water transport (Shen and Tofflemire 1980). In recognition of the potential human health hazard, the Hazardous and Solid Waste Amendments of 1984 require the EPA Administrator to promulgate regulations for the monitoring and control of air emissions at hazardous waste treatment, storage, and disposal facilities. Mathematical models can be used to evaluate emissions of selected volatile chemicals from land treatment operations.

Transport Equation Models

The modeling of emissions to the atmosphere from soil processes has been dealt with by Jury et al. (1983) and Enfield et al. (1985) through the use of transport equations. Their approach is to use equations similar to (25) through (36) without the inclusion of terms for the immiscible phase. Jury et al. (1983) proposed the following "scenario": (1) Uniform incorporation of a chemical to a specified depth, L; (2) Volatilization of the chemical through a stagnant of air just above the soil surface; (3) A steady flux of water into the soil; and (4) An infinite depth of uniform soil below the zone of incorporation. Their scenario closely describes the case of land treatment which leads to the following set of boundary conditions for the transport equation (33).

$$C_T = C_{Ti} \qquad 0 < X < L \text{ for } t = 0 \tag{45}$$

$$C_T = 0 \qquad X > L \text{ for } t = 0 \tag{46}$$

At the upper boundary, the transport of the chemical through the stagnant boundary layer is equal to the flux at the soil surface. Thus,

$$-D_E\,(\partial C_T/\partial X) + V_E C_T = -H_E C_T \quad \text{for } X = 0 \text{ at all } t \tag{47}$$

where H_E is the effective mass transfer coefficient defined by

$$H_E = h/B_v \tag{48}$$

The vapor flux at the surface of the soil is deferred through the following relationship:

$$J(0,t) = -H_E C_T \tag{49}$$

where h (M/D) is the mass transfer coefficient across the stagnant air film. Jury et al. (1983) solved the appropriate transport equations analytically for these boundary conditions, yielding an expression for the vapor flux of organics from soil.

Thibodeaux-Hwang Model

Thibodeaux and Hwang (1982) have also investigated the question of volatile emissions from land treatment. Their approach was to evaluate the transport of volatile chemicals through the soil as an independent process. They assumed no movement of liquids in the soil, no adsorption on soil particles, and no biochemical oxidation of the pollutant. Their approach was based upon their concept of a "dried-out" zone. This concept is illustrated in Figure 11. It is assumed that the soil is contaminated between depths h_s and h_p. As the pollutant evaporates and the vapor diffuses through the soil pores upward to the surface, a

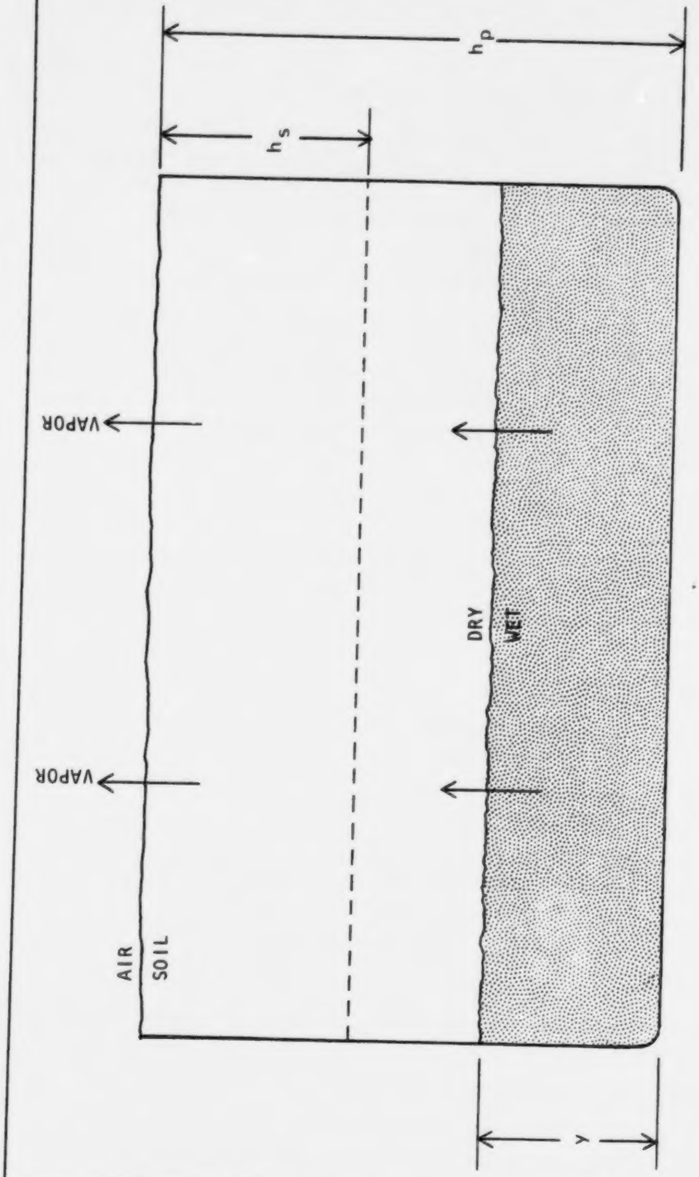
h_p
h_s
VAPOR
VAPOR
AIR
SOIL
DRY
WET
y

FIGURE 11. Thibodeaux-Hwang land treatment volatilization model.

"dried-out" zone quickly develops. If the resistance to mass transfer through the stagnant boundary layer above the soil surface is ignored, the flux through the surface can be expressed as

$$J(0,t) = -D_V C_{wz}/hp\text{-}y \tag{50}$$

Where D (M^2/D) is the effective diffusivity in the air-filled pores and C_{wz} (gm/M^3) is the vapor-phase concentration of the pollutant in the wet zone. Through mass balance relationships and the appropriate boundary conditions the following expression for the flux through the wet-dry interface can be developed.

$$J(0,t) = D_V C_{wz} \sqrt{h_s^2 + 2(hp-hs)\, D_V C_{wz} At/M_A} \tag{51}$$

Where M_A (gm) is the application amount of the pollutant, and A is the soil surface area over which the pollutant is applied. Thibodeaux and Hwang (1982) proceed further to show how equation (51) can be applied to oily waste. They also have compared equation (51) to published experimental results for the evaporation of Dieldrin and Benzene from soil. Their equation predicted vapor fluxes to a reasonable degree of accuracy.

Illustrative Calculations

A comparison of the Jury et al. (1983) model and the Thibodeaux-Hwang (1982) model would be useful. To do this consider the following example where Lindane is applied to the surface of the soil. The following parameters are to be used.

M_A	application rate	1.5 gm
hp	depth of incorporation	0.15 M
ε	total porosity	0.5
ρ	bulk density of the soil	1.35 x 10 gm/M^3
θ	water content	0.3
η	air content	0.2
d	boundary layer thicknessf	0.00462 M
f_{oc}	fraction organic in the soil	0.0125
A	area over which pollutant is applied	1.0 M^2

The following physical-chemical properties of lindane are to be used in the calculations (Jury et al. 1983).

$D_{air,\ v}$	air diffusion coefficient	0.43 M^2/D
$D_{water,\ a}$	water diffusion coefficient	4.3 x 10^{-5} M^2/D
K_{oc}	organic carbon partition coefficient	0.0013 M^3/gm
K_H	Henry's law constant	1.33 x 10^{-4}

Calculations for the Jury et al. model

The solid-liquid partition coefficient K_D can be estimated by

$$K_D = f_{oc}K_{oc}$$
$$K_D = (.0125)(.00130\ M^3/gm)$$
$$K_D = 1.63 \times 10^{-5}\ M^3/gm \qquad (52)$$

Now D_a and D_v can be estimated by use of the Millington and Quirk (1961) models

$$D_v = (\eta^{10/3}/\varepsilon^2)\ D_{air,\ v} \qquad (53)$$

$$D_a = (\theta^{10/3}/\varepsilon^2)\ D_{water,\ a} \qquad (54)$$
$$D_v = (0.2^{10/3}/0.5^2)(0.43\ M^2/D)$$
$$D_v = 8.05 \times 10^{-3}\ M^2/D)$$
$$D_a = (0.3^{10/3}/0.5^2)(4.3 \times 10^{-5}\ M^2/D)$$
$$D_a = 3.11 \times 10^{-6}\ M^2/D)$$

The effective diffusivity is computed using equations (29), (31), and (34).

$$B_v = (\rho K_D/K_H) + (\theta/K_H) + \eta \qquad (55)$$

$$B_v = (1.35 \times 10^6\ gm/m^3)(1.63 \times 10^{-5} m^3/gm) + (0.3/1.33 \times 10^{-4}) + 0.2$$

$$B_v = 167{,}000$$

$$B_a = \rho K_D + \theta + \eta K_H \qquad (56)$$

$$B_a = (1.35 \times 10^6\ gm/m^3)(1.63 \times 10^{-5} m^3/gm) + (0.3 + 0.2(1.33 \times 10^{-4})$$

$$B_a = 22.2$$

$$D_E = (\eta D_G/B_V) + (\theta D_a/B_a) \qquad (57)$$

$$D_E = [(0.2)(8.05 \times 10^{-3}\ m^2/D)/167{,}000] + [(0.3)(3.11 \times 10^{-6}\ m^2/D)/22.2]$$

$$D_E = 5.16 \times 10^{-8}\ M^2/D$$

The effective mass transfer coefficient is computed by equations (48) and (49).

$$h = D_{air,\,v}/d \qquad (58)$$

$$h = (0.43\ M^2/D)/0.00462\ M$$

$$h = 93.1\ M/D$$

$$H_E = h/B_v \qquad (59)$$

$$H_E = 93.1\ (M/D)/167{,}000$$

$$H_E = 5.56 \times 10^{-4}\ M/D$$

The initial total concentration can be determined

$$C_{Ti} = MA/L \qquad (60)$$

$$C_{Ti} = (1.5\ gm/M^2)/0.15\ M$$

$$C_{Ti} = 10\ gm/M^3$$

Now the flux of lindane from the surface can be computed from the Jury et al. model. The results are shown in Figure 12 and 13.

Thibodeaux-Hwang Model Calculations

h_s	subsurface injection depth	0.0 M
h_p	depth of incorporation	0.15 M
D_V	diffusivity of vapor in soil pores	$8.05 \times 10^{-3}\ M^2/D$

C_{wz}, the wet zone vapor concentration of the pollutant, can be computed as

$$C_{wz} = C_{Ti}/B \qquad (61)$$

$$C_{wz} = (10\ gm/M^3)/167{,}000$$

$$C_{wz} = 5.98 \times 10^{-5}\ gm/M^3$$

$$[A(hp\text{-}hs)M_A] = C_{Ti} \qquad (62)$$

$$[A(hp\text{-}hs)M_A] = 10\ gm/M^3$$

The flux of Lindane from the surface can now be estimated from the Thibodeaux-Hwang model. These results are shown in Figures 12 and 13. As can be seen, these two models give very close results except where the time is near zero. This is due mainly to the assumption in the Thibodeaux-Hwang model of zero mass transfer resistance in the air layer above the surface of the soil. At zero time, Thibodeaux-Hwang predicts an infinite flux, whereas Jury et al. predicts a

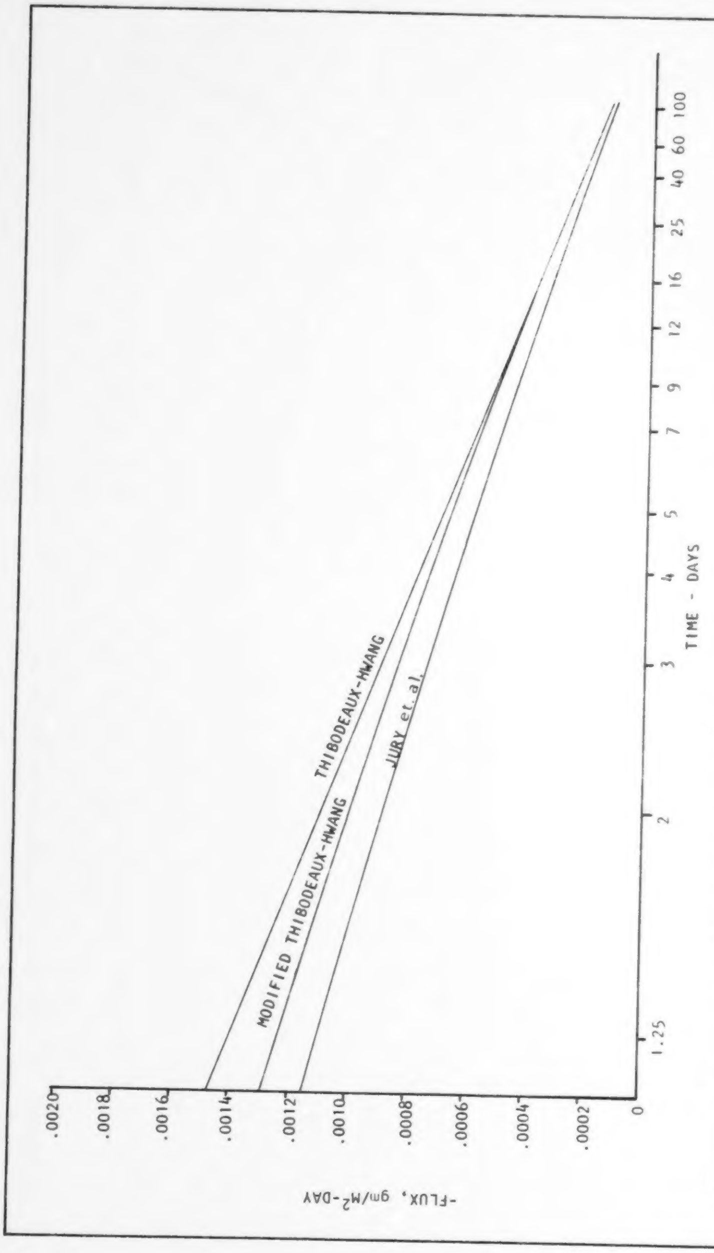

FIGURE 12. Comparison of volatilization models for land treatment at large times.

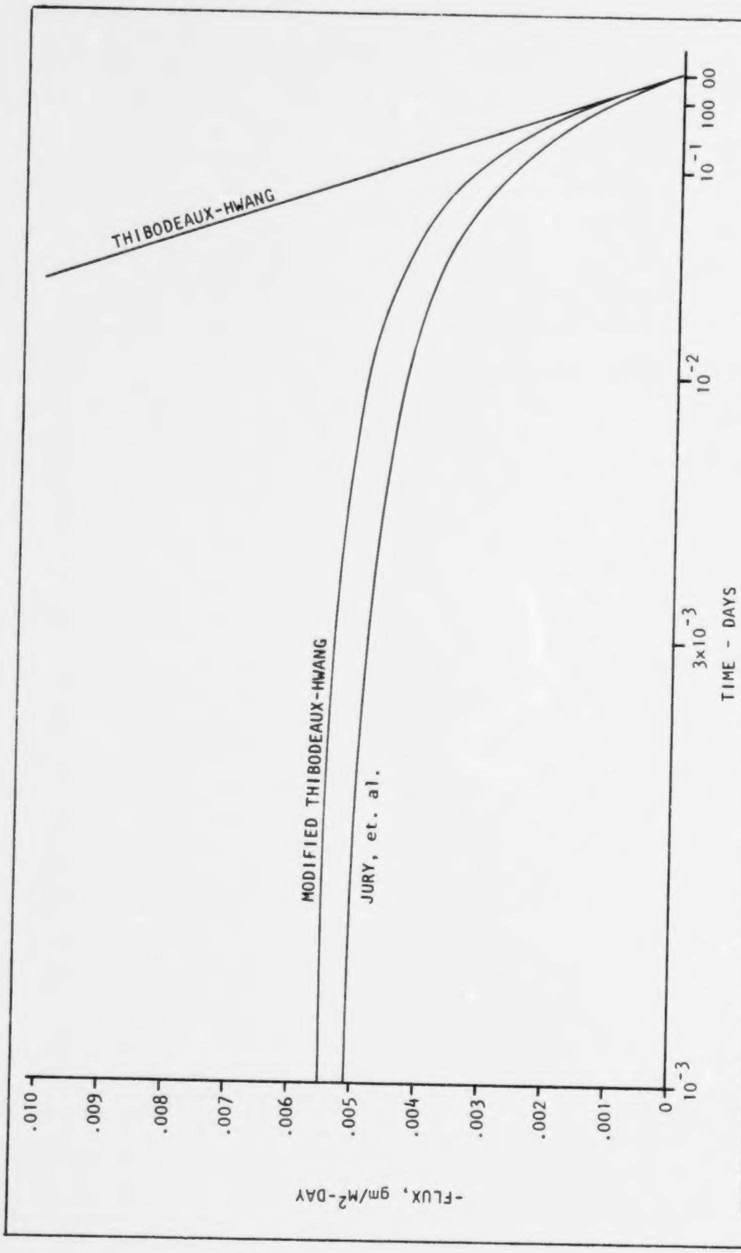

FIGURE 13. Comparison of volatilization models for land treatment at times near zero.

finite flux. The Thibodeaux-Hwang equation can be modified to include a mass transfer coefficient at the boundary layer. The results of this modification are shown below for the case where h = 0 and replacing {A(hp-hs)/M_A} with the equivalent of C_{Ti}.

$$J = D_v C_{Ti}/4th - \sqrt{(D_{2,v} C_{Ti}^2/16t^2h^2) + (D_v C_{Ti} C_{wz}/2t)} \qquad (63)$$

This modification was used to solve the example problem. The results are also included in Figure 12 and 13. As can be seen, the modified Thibodeaux-Hwang (1982) and the Jury et al. models (1983) give results that are very close.

NOMENCLATURE

Symbol	Explanation	Units
A	Soil surface area over which the pollutant is applied	M^2
B_a	Aqueous phase concentration term defined by equation 33	
B_o	Immiscible oil phase concentration term defined by equation 34	
B_s	Soil phase concentration term defined by equation 36	
B_v	Vapor phase concentration term defined by equation 35	
B.N.R.	Base numerical rating defined by equation 46	
C_a	Concentration of pollutant in the aqueous phase	gm/M^3
C_{DL}	Analytical detection limits on concentration in the aqueous phase	gm/M^3
C_i	Maximum concentration in the liquid phase for a or pulse input	gm/M^3
C_o	Concentration in the oil phase	gm/M^3
C_s	Concentration in the soil phase	gm/M^3
C_T	Concentration of the pollutant in the total of all phases	gm/M^3
C_{Ti}	Applied initial total concentration in all phases	gm/M^3
C_V	Concentration of the pollutant in the vapor phase	gm/M^3
C_{wz}	Concentration of the pollutant in the vapor phase of the "wet zone"	gm/M^3
d	Boundary layer thickness of the air just above the surface of the soil	M
D_a	Aqueous phase dispersion coefficient	M^2/D
$D_{water, a}$	Diffusivity of pollutant in water	M^2/D
D_E	Effective dispersion coefficient defined by equation 38	M^2/D

D_o	Dispersion coefficient in the oil phase	M^2/D
D_v	Dispersion coefficient in the vapor phase	M^2/D
$D_{air, v}$	Diffusivity of the pollutant as a vapor through air	M^2/D
erfc	Complementary error function	
f_{oc}	Fraction of soil that is organic carbon	
h	Mass transfer coefficient in boundary layer of air just above the soil surface	M/D
H_E	Effective mass transfer coefficient in boundary layer vapor phase based upon total concentration	M/D
h_s	Subsurface injection depth	M
h_p	Depth of application	M
J	Flux	gm/M^2-D
K_d	Aqueous-soil phase partition coefficient	gm/M^3
K_H	Aqueous-vapor phase partition coefficient, Henry's Law constant	
K_L	Aqueous-immiscible oil phase partition coefficient	
K_{oc}	Organic Carbon Partition coefficient	gm/M^3
L	Length of input pulse	M
M_A	Amount of pollutant applied to soil	gm
P	Pulse function	
R	Retardation factor	
S	Step function	
t	Time	D
$t_{1/2}$	Half-life (first-order)	D
U	Variable defined by equation 22	M/D
V_a	Interstitial velocity of the aqueous phase	M/D
V_E	Effective interstitial velocity of all phases	M/D
V_o	Interstitial velocity of the immiscible oil phase	M/D
V_p	Interstitial velocity of the pollutant	M/D
V_v	Interstitial velocity of the vapor phase	M/D
X	Distance, usually depth	M
Y	"Wet zone" depth	M
Z	Depth of the treatment zone	D
β	Ranking factor for principal hazardous constituents	1/D
ε	Total porosity	M^3/M^3
η	Volumetric air content of the soil	M^3/M^3
θ	Volumetric water content of the soil	M^3/M^3
μ_a	First-order reaction rate constant in the aqueous phase	1/D
μ_E	Effective first-order reaction rate constant in the phases defined by equation 39	1/D

μ_o	First-order reaction rate constant in the immiscible oil phase	1/D
μ_s	First-order reaction rate constant in the soil phase	1/D
μ_v	First-order reaction rate constant in the vapor phase	1/D
μ	First-order reaction rate constant for the combined phases	1/D
μ	Average first-order reaction rate constant for the combined phases assuming equal reaction rate constants for each phase	1/D
ρ	Bulk density of the soil	gm/M^3
ϕ	Volumetric immiscible oil phase of the soil	M^3/M^3

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MODELING OF PROCESSES IN THE SATURATED ZONE

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INTRODUCTION

The goal of groundwater modeling as applied to land treatment processes is to predict the solute transport behavior of a chemical species from the time it reaches the aquifer to the time it interfaces with the biosphere. Of importance are where and when the solute reaches the interface, and at what concentrations. The first question that comes to mind concerns why saturated zone models have any importance in land treatment. In an operating system that is well designed and controlled, the waste should not reach the aquifer at undesirable concentrations. However, if something should go wrong with the system, these models provide a framework for predicting the impact of the waste release on human health and the environment. In general, groundwater modeling has an application in the tasks of forecasting transport behavior, development of management and design alternatives, and in field parameter identification. In the area of management, groundwater models can act as a screening tool when combined with chemical characteristics of specific wastes applied in land treatment. The application of groundwater models for saturated flow conditions is reviewed in this paper.

MODELING FRAMEWORK

Modeling of solute transport in saturated groundwater systems is much more difficult than the more classical task of modeling groundwater hydraulics. In this latter task the basic questions concern yields and drawdown. These questions are addressed without regard to where the water comes from. However, for solute transport models, one is intimately concerned with where the solute goes, how long it takes to get there, and with the various physical, biotic, and abiotic processes the solute experiences along this flow path. For these reasons, and because the field of solute transport modeling is of rather recent development, successful applications of solute transport models are not as common as those of hydraulic models.

A large number of groundwater models have been developed and presented in the literature. Many of these are reviewed, with a discussion of their use and limitations, in the monograph by van der Heijde, et al. (1985). No specific models are discussed herein; only the general features common to all models are highlighted.

The basic framework of solute transport models is the mass balance principle. This principle says, that for any region of space, the following balance holds:

$$\begin{array}{ccccccc} \text{the rate} & & \text{the flux} & & \text{the flux} & & \text{the rate} \\ \text{of mass} & = & \text{of mass} & - & \text{of mass} & + & \text{of mass} \\ \text{increase} & & \text{in} & & \text{out} & & \text{generation} \\ & & & & & & \text{(reactions)} \end{array}$$

The rate of mass increase or storage includes the mass in the mobile pore space fluid, the mass sorbed on the porous matrix, and the mass immobilized by precipitation, uptake, or fixation. The fluxes in and out of the region involve the physical processes of advection and mixing. The mass generation includes biotic and abiotic reactions. These processes are discussed in more detail below.

The heart of the modeling process is the translation of the mass balance principle into a mathematical model. It is from this mathematical model that quantitative assessments are drawn. The mass balance principle itself takes the form of a partial differential equation. This equation may be coupled with algebraic equations which express chemical equilibrium relations. In addition, if there is more than one interacting chemical species, there is a mass balance equation for each. The entire system of differential and algebraic equations presents a formidable set which in general defies application of analytical mathematical techniques for solution. Thus, one usually attempts to solve the solute transport problem using numerical methods.

The digital computer is not able to solve differential equations. Thus, in order to attempt a numerical solution of the solute transport problem, the next step is to translate the mathematical statement of the problem into an approximating set of algebraic equations, which the computer can attempt to solve. The result is usually a system of coupled nonlinear algebraic equations, for which further approximations are applied to obtain the "solution." As such, the modeling process is extremely difficult and complex. Nevertheless, the problem is well studied and techniques are available to obtain desired accuracy and assess errors. While a great deal of experience and art may be required, mathematically, the transport problem is "solvable."

PHYSICAL PROCESSES

The solute transport model rests on the principle of mass balance. The transport processes which it describes include the physical processes of advection and mixing. Advection refers to the transport of a solute as it is carried along with the groundwater flow. It is apparent then, that in order to obtain an accurate estimate of advective transport, one must first obtain an accurate estimate of the groundwater flow field. Thus transport modeling inherently includes hydraulic modeling.

Mixing refers to the dilution of a solute as it mixes with surrounding groundwater. Two processes account for this. Even in the absence of advection (bulk groundwater movement), mixing occurs through the process of diffusion. Diffusion is a manifestation of the random motion on a molecular scale due to thermal energy. This transport is described by Fick's Law which states that the solute always moves from regions of higher concentration toward regions of lower concentration. The rate of transport is proportional to the concentration gradient. Diffusive transport is slow, and if diffusion was the only mixing process, it is unlikely that mixing would be considered of importance in solute transport modeling. However, there is an additional process when there is bulk groundwater movement, and this process usually dominates diffusion, at least in shallow groundwater systems. This is the process of dispersion.

If there is bulk groundwater movement, then two fluid particles which are at one time close together may move further and further apart as they migrate through different pores and at different speeds. This spreading of a collection of fluid particles is a type of mixing associated directly with the presence of bulk motion and the complex porous matrix. The process of macroscopic scale mixing is called mechanical dispersion, and it usually exceeds the effects of diffusion in shallow groundwater systems. Mechanical dispersion is usually modeled as a Fickian process with the amount of mixing greater in the direction of flow than transverse to that direction. Mechanical dispersion is described by a tensoral dispersion coefficient while diffusion is described by a scaler diffusion coefficient. It is common practice to combine both of these coefficients into a single coefficient describing the combined hydrodynamic dispersion.

CHEMICAL AND BIOTIC PROCESSES

The chemical and biotic reactions which are of importance to land treatment of hazardous wastes have already been discussed at this symposium. These are summarized in Table 1. Reactions may be classified into two groups. The first consists of those which are sufficiently fast and reversible. For these, thermodynamic equilibrium relations may be used. The second group consists of those which are insufficiently fast and/or irreversible. For this second group, chemical kinetic models are used. A subclassification for each group consists of those reactions which are homogeneous (occur in a single phase) and those which are heterogeneous (involve more than one phase). An additional classification of heterogeneous reactions considers those which occur at the surface of the porous matrix, and those classical chemical reactions which result in the production or consumption of a separate phase. This classification scheme was presented by Rubin (1983) and is expedient for discussing how different types of chemical reactions enter in the mathematical statement of a solute transport problem.

An alternative classification scheme considers how the chemical and biotic reactions enter into the transport and fate behavior of a solute. This classification based on transport and fate behavior is shown in Table 2. The resulting processes are of interest, rather than the specific reactions involved. The physical processes include advection, diffusion, and dispersion. As has already been discussed above, advection refers to the bulk movement of the solute with the groundwater flow. Diffusion and dispersion result in a decrease in solute concentration as it moves along its flow path because of dilution with ambient groundwaters. Degradation refers to the decrease in solute concentration because of chemical or biotic reactions. The term immobilization is self-explanatory. A species is immobilized when it precipitates, becomes fixed to the porous matrix, or, in the case of multiphase flow of an organic species, when it reaches its residual saturation. In this latter case, the solute may still migrate as a dissolved species in the water phase. Retardation refers to the slowing in rate of migration, as compared with the groundwater flow, because of surface interactions. Bioaccumulation and volatilization are generally not of importance for solute transport in the saturated zone.

This second classification scheme is useful for discussions of transport and fate modeling, for example in the use of groundwater models as screening tools for hazardous waste application during land treatment. As a screening tool, a worst-case scenario would be considered. For land treatment this would involve a constant application rate of the solute and a steady-state mathematical model. The only transport and fate processes of interest would be dispersion and degradation. Advection is important only in determining where the solute goes and its travel time. A species which experiences retardation has a longer travel time and thus a longer time for degradation, and thus retardation is of indirect importance. If the decrease in concentration due to dispersion and degradation results in an acceptable concentration at the interface with the biosphere, then such a land application would be considered acceptable. Otherwise, further scrutiny is required.

TABLE 1. Classification of biotic and abiotic reactions.

	Equilibrium Reactions	
Homogeneous	Surface	Classical
complexation	sorption	precipitation
acid/base	exchnage	dissolution
hydrolysis	bioaccumulation	redox
redox		acid/base
	Kinetic Reactions	
Homogeneous	Surface	Classical
complexation	sorption	precipitation
acid/base	exchange	dissolution
hydrolysis	biodegradation	redox
radioactive decay		acid/base
substitution		

TABLE 2. Classification of transport and fate processes.

Physical	Biotic and Abiotic
advection	bioaccumulation
diffusion	degradation
dispersion	immobilization
	retardation
	volatilization

APPLICATION OF SOLUTE TRANSPORT MODELS

As noted in the introduction, there are three types of applications of solute transport models: forecasting transport behavior, development of management and design alternatives, and field parameter identification. When models are applied in the investigation of a specific field site, all three applications find use.

Ideally, a modeling effort involves the three steps of calibration, verification, and prediction or forecasting. During the calibration phase, modeling and monitoring go hand in hand. Monitoring assesses the geologic, hydrologic, and chemical characteristics of a site. This involves the drilling of observation wells, geologic core and chemical sampling, and hydrologic testing. A mental picture of the system is developed. This mental picture can be tested with a mathematical model with model results compared with actual field observations. Uncertainties are highlighted and further monitoring is suggested. The groundwater flow model is calibrated by adjusting hydraulic conductivity values and sometimes flow rates at boundaries, sources, and sinks, until the model simulates the observed heads. Groundwater velocities are calculated using Darcy's Law. The solute transport model is calibrated for a conservative solute by adjusting dispersivities and sometimes porosity until the model simulates the observed concentrations. Finally, for a reactive solute, the transport model is calibrated by adjusting chemical parameters (rate constants, distribution coefficients) until the model simulates the observed concentrations. During this trade-off between modeling and monitoring, the model is calibrated to the site.

Verification involves the application of the calibrated model to a new and independent record of field behavior. If such a record exists, and if the model simulation results correspond satisfactorily to the measured field performance, then the model can be used with some confidence for prediction or forecasting and the development of management strategies.

LIMITATIONS ON THE "STATE OF THE ART"

As noted above, mathematically, the modeling problem is solvable. Given a large computer and a sufficient budget, one can simulate solute transport to whatever level of accuracy is desired. The real difficulty comes in with development and interpretation of field data. A numerical model requires values for hydraulic and chemical parameters for each node or cell in the model. These values have to be estimated from a relatively small amount of field data which is fairly expensive to obtain. Further, the parameters in the model represent spatially averaged parameters which may not be directly related to field tests. There is no unique solution of the parameter identification problem and a great deal of interpretation is required.

The verification phase of solute transport modeling is almost never carried out. All existing data is generally used during the calibration phase. It is unlikely that one would repollute the aquifer to test a model. Thus one goes directly from calibration to prediction.

A further problem is that some of the processes are poorly understood. For example, dispersion in the laboratory is well studied and rests on a firm theoretical foundation. In the field, however, that parameter which characterizes dispersion, the dispersivity, has a magnitude which is several orders of magnitude larger than that measured in the laboratory. The magnitude of the field dispersivity depends on the size of the region studied, rather than being a characteristic constant of the aquifer (Anderson 1984). While one can interpret these results by considering field dispersion as caused by the complex flow through the heterogeneous geologic media just as laboratory dispersion is caused by the complex flow through the pore structure of the homogeneous media, no adequate theory exists for predicting field scale dispersion. The subject has been of great interest in current research, and one may anticipate further development in our understanding and quantification of field scale dispersion.

Just as in the case for dispersion, there is a great deal of uncertainty in our understanding of chemical and biotic processes. A basic question concerns the use of equilibrium or kinetic models. While a great deal of data exists for equilibrium models, data for rate constants for kinetic models is sparse and uncertain. The relative importance of various reactions, especially those concerning biotic processes, is also largely unknown. Chemical models often assume homogeneous chemical and biotic fields, while field experience suggests a nonuniform distribution of sorption sites, mineral phases, and microenvironments which change in their chemical nature over short distances. As research and field experience progresses, these uncertainties will gradually be addressed.

Finally, there is the difficulty in characterizing and quantifying the complex geology which typifies most field sites. It is uncertain at what scale sampling is required for field data to be used in modeling. Heterogeneities are averaged out for modeling, and the complex three dimensional flow pattern appears as a simplified two dimensional flow. The effects thereof on modeling are unknown.

In summary, mathematically we are well advanced in our modeling potential. In practice, however, we lack an adequate understanding of certain important processes. Solute transport modeling of a specific site will remain just as much an art, as a science or engineering discipline, for the forseeable future.

PRACTICAL UTILITY OF GROUNDWATER MODELS

Given our relatively poor status in the practical application of groundwater solute transport modeling, one may question the utility of the increasing effort which goes into the further development of groundwater models, as well as the utility of our existing models. Fortunately, groundwater models are very good for answering "what if" questions: given such and such a site with such and such characteristics, what would happen if we did this or that? The closer the chosen characteristics are to those of an actual site, the closer the simulation corresponds to reality. Regardless, the experience gained through analysis of sensitivity can be used to develop an intuition for how an actual site may respond to various management strategies.

It appears that groundwater solute transport models will play a major role in the EPA's development of a decision rule for restricting hazardous wastes from RCRA land disposal units. The basic idea here is that an acceptable concentration (the Acceptable Daily Intake for a noncarcinogen or the Virtually Safe Dose at 10^{-6} risk level for a carcinogen) is fixed at a point of contact with the biosphere (say a well down-gradient from the facility) and the influent leach concentration which would result in this concentration is back calculated. The model itself takes into account the effects of dilution due to dispersion, as well as degradation and retardation. Such a model could be applied on a generic basis or on a site by site basis using representative data. The calculated influent concentration may then be used in the development of a management strategy for that waste.

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CURRENT RESEARCH AND STUDIES HAVING APPLICATION TO LAND TREATMENT OF HAZARDOUS WASTE*

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INTRODUCTION

Land treatment offers a potentially cost-effective and environmentally acceptable management alternative for selected hazardous waste. There is at present, however, a serious lack of verifiable information relative to the successes and/or failures of land treatment systems. The most glaring information gaps pertain to the transport and fate of organic hazardous constituents within the complex waste-soil matrix. Until such information becomes readily available to regulatory decision makers, land treatability decisions will be conservative and, in many cases, potentially could be unduly restrictive.

Research and demonstration (R&D) activities directed toward filling the identified information deficiencies provides the key to the future of land treatment technology as an acceptable management alternative for hazardous and other industrial wastes. It is only through well organized, scientifically designed R&D studies that the comprehensive technical information base needed to make informed decisions pertaining to land treatment banning and permitting, as well as to the location, design, and operation of individual land treaument units, can be generated.

Basic land treatability information needs are encompassed within four major areas of interest [Resource Conservation and Recovery Act (RCRA) and Amendments, 1976 and 1984]: (a) degradation/transformation of hazardous organic waste constituents, (b) immobilization/transport of hazardous inorganic and organic waste constituents, (c) potential for impact (toxicity) of waste constituents on human health and the environment, and (d) propensity to bioaccumulation of hazardous organic and inorganic waste constituents. The diversity of these areas of interest provides the impetus for conducting and/or funding hazardous waste land treatment (HWLT) R&D activities that will help to fill information gaps and

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build the scientifically derived data base needed to make informed land treatability decisions.

There are numerous R&D activities underway that will help to establish the required data base. The purpose of this paper is to identify those responsible for supporting land treatment related R&D activities, to present an overall synopsis of current efforts, and to highlight some of the major studies of interest to the user community including those involved with making land treatment decisions.

RESEARCH AND DEMONSTRATION COMMUNITY

Several governmental agencies and specific industrial groups are involved in R&D studies of interest to the HWLT user community. Most of the projects within this overall R&D effort, while supported by governmental and/or industrial funds, are conducted by the academic and consulting communities.

Industrial Community

Industrial groups and specific representatives within such groups support R&D activities that provide input to the overall HWLT technical data base. The groups which are currently the most active represent the petroleum and wood preserving industries: (a) American Petroleum Institute (API), (b) The Petroleum Association for Conservation of the Canadian Environment (PACE), and (c) Southern Pressure Treaters Association (SPTA). Segments of the chemical industry, i.e., Pesticide Applicators Association, also are interested in land treatment and are supporting some R&D activities on specific wastes and their hazardous constituents.

Although the petroleum and wood treating industries are the primary supporters of R&D efforts in the HWLT arena, several other industrial categories are involved in R&D efforts for wastes not currently listed as hazardous. These include: (a) leather tanning, (b) coal gasification/liquefaction, (c) electric power, (d) mining, (e) food processing, (f) pulp and paper. Such efforts can contribute to the overall state of the knowledge pertaining to land treatment technology as a management alternative for selected industrial wastes.

Governmental Agencies

The Environmental Protection Agency (EPA) serves as the focal point for Federal environmental R&D activities. The EPA, however, is not the only Federal agency supporting studies that are helping to build the comprehensive land treatment data base needed to make the most efficient use of the waste management alternative. Other agencies involved include: (a) Department of Agriculture (USDA), (b) Department of Energy (DOE), (c) Department of Defense (DOD), and (d) United States Geological Survey (USGS). Additionally, Canada and European countries as well as many state agencies support studies related to land disposal of hazardous waste which can provide an important input to the HWLT data base.

RESEARCH AND DEMONSTRATION ACTIVITIES

Industry

Petroleum. The petroleum industry has a long history of supporting studies pertaining to land treatment of petroleum wastes. Two relatively recent comprehensive reports that were supported by the API provide a synopsis of most of the information developed during previous studies supported by the industry (1,2).

The latest of these reports, which addresses Appendix VIII constituents contained in oily wastes, concludes that all such organic constituents which may be present in land treated petroleum wastes can be degraded in soil under proper management conditions before they can migrate below the treatment zone (2). This conclusion is based primarily on literature data from carefully controlled laboratory and/or bench-scale studies, many of which were conducted using single compounds mixed in either soil or a soil/nutrient solution. Unfortunately, there still remains a scarcity of documented information relative to the degradation kinetics and transport parameters for these organic hazardous constituents within the complex oily waste-soil matrix found in land treatment units. There is even less monitoring data that has been generated over a long enough period of time from actual operating facilities that will verify environmentally acceptable treatability of these constituents in land treatment units.

The API, recognizing that these information deficiencies are real, is initiating an R&D effort involving laboratory treatability studies of hazardous organics for different wastes and soils. The API is also currently involved in a cooperative project with EPA pertaining to environmentally acceptable closure techniques for land treatment sites. Actual work on the closure project is being performed by Law Engineering, Marietta, Georgia.

PACE also has supported two reports which address the subject of land treatment of petroleum industry sludges (3,4). The 1983 report dealing with the significance of trace substance in land treatment sites concluded that, based on the current information available, positive degradation of all classes of organics found in land-applied petroleum wastes takes place under suitable conditions with sufficient time (4).

The report also notes, however, that: (a) quantitative information on the fate of trace organic substances in petroleum land treatment sites is limited; (b) insufficient data is presently available to assess the toxicity of leachates and runoff because the petroleum sludges are poorly characterized with regard to trace organics; (c) more data is needed to determine if groundwater quality has been impaired, and (d) the effect on site life and contaminant releases of long-term organic residues produced in the degradation process is not presently understood. In recognition of these information deficiencies, PACE is currently supporting a research effort to identify and quantify trace organics in three types of land-applied refinery sludges.

Several individual companies within this industrial group also support R&D activities directed toward generating information specifically related to land treatment of refinery sludges. Two of these which have supported such activities over a long period of time are CONOCO and Sun Marketing and Refining Company.

Wood Preserving. The wood preserving industry has for some time been supportive of land treatment R&D activities relative to spray and trickle irrigation of wastewaters and land application of wastewater treatment sludges. Results from these studies indicate that wood preserving wastes can be degraded in the soil under proper conditions given sufficient time. Again, however, insufficient quantitative data is available on the degradation kinetics and transport parameters for individual organic hazardous constituents within the complex waste-soil matrix found in land treatment units.

The presence of polynuclear aromatic hydrocarbon (PAH) compounds in groundwater underneath wood preserving waste storage lagoons dictates the need for a scientifically-derived transport and fate data base for use in making land treatability decisions pertaining to such wastes. This need has been recognized by the SPTA, individual corporations having wood preserving activities and the railroad industry. At present, soil treatability studies pertaining to organic hazardous constituents contained in these wastes are being sponsored by each. Additionally, the SPTA is actively supporting a comprehensive cooperative R&D study between Mississippi State University and the EPA to determine the efficacy of using land treatment as a management alternative for wood preserving wastes.

Leather Tanning. There is a high degree of interest within the leather tanning industry to use land application for management of selected waste streams emanating from tannery operations. Currently, a cooperative study between the Tanners' Council and the EPA involving land treatment of two of these waste streams is nearing completion. Although tannery waste streams have been delisted, results from this five-year field study will provide valuable input to the overall land treatment data base.

Coal Gasification/Liquefaction. Although wastes from this industry are not listed as hazardous, the wastes produced are similar in content to those produced from creosote wood preserving operations. Principal organic waste constituents are the PAH compounds. Ongoing studies of interest to the HWLT user community are those pertaining to soil treatability and bioaccumulation of hazardous constituents.

Electric Power. The Electric Power Research Institute as well as several individual electric power companies are supporting R&D efforts that are examining the environmental effects of potentially toxic wastes resulting from coal-fired generating plants. Most of these studies pertain to assessing the potential use of fly ash in agricultural systems or the use of recycled cooling water on the land for irrigating various crops. In either case, information being developed is primarily in the areas of toxicity and bioaccumulation of inorganic constiuents such as metals and fluoride.

Mining. The National Coal Association supports R&D activities relative to the reclamation and revegetation of stripped mining lands. Information from these studies may prove beneficial to the HWLT user community for the purpose of closing land treatment sites in an environmentally acceptable manner.

Food Processing. Land treatment technology is widely utilized as a management alternative for wastewater and residuals generated by various segments of the food processing industry. The general information developed relative to the location, design, operation/management, and monitoring of land treatment units provides the most important benefits to the HWLT user community.

Pulp and Paper. Various segments of the pulp and paper industry also use land treatment technology as a management alternative for waste residuals. In addition to the general information relative to the location, design, and operation/management of land treatment units, data pertaining to degradation kinetics and transport parameters for specific organic waste constituents provide a potential input to the overall HWLT data base.

Government

State. Many states support some R&D activities related to the safe and effective disposal of industrial waste residuals on land. A prime example is the state of Oklahoma which recently let a contract for a study which addresses the land treatment of petroleum drilling pit wastes. Such studies can be a good source for input to the comprehensive technical data base needed for land treatment technology. The major problem that exists, however, is that the information often is reported only to the state agency that requests it and never reaches the open literature. Some mechanism must be established to make such information readily available to the user community.

Foreign

Western Europe. Several countries within the western European community have regulations which allow land application of industrial wastes in such quantities that do not constitute a risk to health or the environment. As an example, most countries specifically prohibit the uncontrolled disposal of oily sludge with the disposal of such sludge usually permitted at local authority level (5). As within the United States, the primary thrust of this effort is to protect the groundwater against pollution by dangerous substances.

Many current or completed R&D studies pertain to land application of oily sludges. Usually these studies are conducted as a cooperative effort between the oil companies international study group for Conservation of Clean Air and Water, Europe CONCAWE, and the Departments of Agriculture or Biology of universities or government agencies.

Canada. Environment Canada supports R&D activities pertaining to land application of both municipal and industrial sludges on land. The Wastewater Technology Centre, Environmental Protection Service, Burlington, Ontario, has a group specifically dedicated to conducting studies relative to land treatment of oily sludges.

Alberta Environment is actively engaged in conducting and supporting R&D studies pertaining to land disposal of industrial waste. The groups actively involved in conducting such studies are located at the Alberta Environment Center, Vegreville, Alberta.

Federal

Department of Agriculture. The USDA at one time supported a major effort pertaining to land treatment of industrial wastes. A comprehensive publication on the subject was authored by scientists from the USDA research facility, Beltsville, Maryland (6).

Recent reductions of R&D funds has curtailed specific USDA land treatment research activities; however, some studies of interest are still being conducted. Current projects related to plant uptake of metals and the fate of pesticides in soils will provide data to input the HWLT technical information base.

Department of Defense. The DOD has ongoing activities within both the Air Force and Army which can provide input to the HWLT data base. The principal Air Force activities of interest relate to the transport and fate of organic pollutants, i.e., TCE, in groundwater. Several of these activities are being conducted in cooperation with the EPA.

The Army supports research activities related to the transport and fate of organic waste constituents in soil and the uptake of dredge spoil constituents by plants and animals. The former is managed by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Edgewood Arsenal, Maryland, while the latter is managed by the Corps of Engineers, Waterways Experiment Station, Vicksburg, Mississippi.

Department of Energy. The DOE supports the operation of several contract laboratories at which R&D studies are being conducted that will generate data that can input the HWLT data base. Most of these studies pertain to wastes resulting from synfuels development. Organic constituents found in these wastes are similar to those found in wastes generated by the petroleum and wood treating industries, i.e., volatile organic constituents (VOC), PAH compounds and phenolics. The areas of study include transport, fate, toxicity and bioaccumulation of these constituents in the terrestrial environment. Results from these studies provide a good potential input source to the HWLT data base.

Geological Survey. The USGS has supported groundwater monitoring efforts for a long period of time. The effort recently has been increased. Information pertaining to monitoring methodology as well as groundwater quality provides a useful input to the overall HWLT data base.

Environmental Protection Agency. Although several EPA laboratories are involved in R&D activities which provide input to the HWLT data base, the Agency has established a specific R&D program dedicated to HWLT at the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma. The primary objective of this program is to develop and verify a comprehensive technical data base for land treatment as a hazardous waste management alternative. The following paragraphs summarize the HWLT research being conducted at the respective EPA laboratories.

1) *Hazardous Waste Engineering Research Laboratory, Cincinnati, OH* (HWERL)—Of particular interest to the HWLT user community is research managed by the HWERL which has the management responsibility for the Agency's R&D activities pertaining to all designated hazardous waste land disposal categories other than land treatment such as landfills, and surface impoundments. Some of the information generated pertaining to the location, design, operation, management, closure, and environmental impact of these facilities also will be relevant to the HWLT data base. Also of interest are HWERL managed studies that provide information relative to the establishment of environmentally acceptable remedial action alternatives at superfund sites.

2) *Environmental Research Laboratory, Corvallis, OR* (CERL)—The CERL supports research activities related to the ecological impacts of pollutants on the terrestrial environment. The work pertaining to biological assessment at hazardous wastes sites will provide input to the HWLT data base in the area of toxicity. Some of the same methodology may be useful for determining when reapplication can be made and/or when detoxification has taken place following closure. Additional work of interest is related to plant uptake of various pollutants.

3) *Environmental Research Laboratory, Athens, GA* (ERL-Athens)—The ERL-Athens supports research activities pertaining to the transport and fate of pesticides in the environment. The data and subsequent transport models developed from these studies provide a valuable input to the HWLT data base.

4) *Environmental Monitoring and Support Laboratory, Las Vegas, NV* (EMSL-LV)—The EMSL-LV has the primary Agency responsibility for developing unsaturated zone and groundwater monitoring methodology. Since both types of monitoring are required at HWLT sites, the information developed is of high interest to the HWLT user community.

5) *Program Offices*—The EPA Program Offices support short-term contract studies to satisfy specific programmatic needs relative to regulation development and implementation. The Office of Solid Waste (OSW) supports activities pertaining to development of hazardous waste guidance documents and analytical methodology. Prime examples of these activities are development of the toxicity extraction (EPII) procedure and the Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations (7). The Office of Air Quality Planning and Standards (OAQPS) has the responsibility for setting air quality standards for HWLT sites and are supporting studies to develop data on air emissions from such sites.

6) *Robert S. Kerr Environmental Research Laboratory, Ada, OK* (RSKERL)—The primary mission of the RSKERL is to manage R&D activities pertaining to pollutant activity in the subsurface environment. Particular emphasis is directed toward the transport and fate of pollutants in groundwater and land treatment of hazardous wastes. Since one of the major concerns about HWLT is adequate protection of groundwater resources, information pertaining to transport and fate of hazardous constituents in the saturated zone provides a needed addition to the HWLT data base.

The primary goal of the HWLT Research Program is to develop and verify the diverse, comprehensive technical data base needed for decision-making relative to land treatability of specific hazardous wastes. Results will be used to provide guidance to permit writers and applicants to insure that land treatment units are located, designed, operated, monitored, and closed in a manner that will insure adequate protection of groundwater resources and the environment.

The EPA, as required by the Resource Conservation and Recovery Act of 1976, promulgated Interim Final Standards applicable to owners and operators of new and existing land disposal facilities and the corresponding procedures for permit applications on July 26, 1982 (CFR Vol. 47, No. 143). Part 264, Subpart M provides standards and permitting procedures applicable to land treatment units. The technical data base necessary to satisfactorily implement these regulations is presently incomplete, with much of the data that is available not having been verified. The need for establishment of this data base was amplified with passage of the Solid and Hazardous Waste Amendments of 1984. These amendments require EPA to set air standards for land disposal methods such as land treatment facilities, within 30 months of passage and to make banning decisions relative to listed hazardous wastes within several specified time periods, the earliest of which is 24 months. All decisions must be made within 66 months of passage. Not only will existence of a diverse comprehensive technical data base facilitate implementation of the Part 264, Subpart M standards, but it also will prove useful in air standards development and the decision making process for banning.

The HWLT R&D activities at RSKERL include the design and implementation of laboratory, bench, and pilot-scale land treatment experiments and field studies that address degradation/transformation, immobilization/transport, toxicity, and the propensity to bioaccumulate for hazardous constituents contained in both listed and nonlisted hazardous wastes. Specifically, these studies are designed to generate data pertaining to: (a) waste characteristics, (b) fate and effects of waste mixtures, (c) loss rates for organic hazardous constituents, (d) soil amendments, (e) cooxidation, (f) soil accumulation of metals, (g) detoxification of waste mixtures, (h) air emissions, (i) soil transport and migration of toxic chemicals, (j) optimum waste loading rates and frequencies, (k) effectiveness of unsaturated zone monitoring procedures, (l) treatment zone limitations, (m) bioaccumulation of waste constituents, (n) closure approaches, (o) formation of hazardous waste degradation intermediate products, (p) use of on-site and/or in situ land treatment for remedial action, and (q) development/verification of predictive models for use in making land treatability decisions.

The history of the RSKERL HWLT Research Program activities since the program inception is presented in Table 1. Research activities, Principal Investigators, RSKERL Project Officers, and past and planned output dates are included. Seventeen of these activities, which will result in 22 planned outputs, currently are in progress. The key outputs for each completed and ongoing research activity are presented in Table 2. Each output is cross-referenced to the EPA need which precipitated the research activity.

TABLE 1. History of HWLT research program activities (U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory).

Research Activity	Contacts	Output Date
1. Land Farming Air Emissions (Task 210)	Eldon Rucker, American Petroleum Institute John Matthews, RSKERL	11/84
2. HWLT Site Selection (Task 224)	Dr. Wallace Fuller, University of Arizona Dr. Don Kampbell, RSKERL	06/84
3. Land Treatment Technology Development for Hazardous Wastes (Task 214)	Dr. Bill Tillman, East Central Okla. University	06/84
4. Use of Bioassays to Evaluate Environmental Impact of Industrial Waste Land Treatment (Task 220)	Dr. K. W. Brown, Texas A&M University John Matthews, RSKERL	08/84
Use of Bioassays to Evaluate Unsaturated Zone Monitoring Procedures (Task 226)	Dr. K. W. Brown, Texas A&M University John Matthews, RSKERL	08/84
5. Closure Evaluation for Petroleum Residue Land Treatment Sites (Task 209)	Dr. James Robertson, University of Oklahoma Dr. Don Kampbell, RSKERL	09/84
6. Land Treatment of Petroleum Refinery Sludges (Task 212)	Dr. Leale Streebin, University of Oklahoma Dr. Don Kampbell, RSKERL	11/84
7. HWLT Microbial Degradation Kinetics (Task 223)	Dr. Don Kincannon, Oklahoma State University Dr. Tom Short, RSKERL	12/84
Summation of Currently Available Land Treatability Screening Procedures (Task 228)	Dr. Don Kincannon, Oklahoma State Universtiy Dr. Tom Short, RSKERL	05/84
8. Screening Terrestrial Bioassay (Task 237)	Dr. Lee Rogers, Battelle Northwest Bill Miller, HMAT Corvallis, EPA John Matthews, RSKERL	12/84
9. Effects of Land-Applied Industrial Wastes on Soil Biota (Task 215)	Dr. R.C. Loehr, Cornell University John Matthews, RSKERL	12/84

TABLE 1. Continued.

Research Activity	Contacts	Output Date
10. Evaluation of HWLT Unit Operational Procedures (Task 235)	Dr. M. K. Mazumder, University of Arkansas at Little Rock Marvin L. Wood, RSKERL	04/85
11. Land Treatment of Ignitable and Corrosive Wastes (Task 232)	George Reid, University of Oklahoma Don Clark, RSKERL	08/85
12. Land Treatment of Tannery Wastes (Task 222)	Dr. Robert Lollar, Tanners' Council of America	08/85
13. Landfarm Closure Study (Task 211)	Eldon Rucker, American Petroleum Institute Fred Pfeffer, RSKERL	09/85
14. Volatilization of Hazardous Compounds at HWLT Site (Task 234)	Dr. Ryan DuPont, Utah State University	10/85
15. Screening Test Battery for Determining Land Treatability (Task 230)	Dr. Wallace Fuller, University of Arizona John Matthews, RSKERL	12/85
16. Effectiveness of Soil Core/ Soil-Pore Liquid Monitoring Procedures (Task 227)	Dr. K. W. Brown, Texas A&M University Fred Pfeffer, RSKERL	12/85
17. HWLT Conference (Task 239)	Dr. J. F. Malina, Jr., University of Texas John Matthews, RSKERL	04/84 12/85
18. Evaluatioin of Specified HWLT Unsaturated Zone Monitoring Protocol (Task 233)	Dr. James Robertson, University of Oklahoma Dr. Don Kampbell, RSKERL	12/85
19. Effects of Loading on Organics Degradation and Migration (Task 236)	Dr. Ron Sims, Utah State University John Matthews, RSKERL	12/85
Evaluation of High Intensity Land Treatment (Task 235)	Dr. Ron Sims, Utah State University John Matthews, RSKERL	05/85
Land Treatability Banning Evaluations (Task 244)	Dr. Ron Sims, Utah State University John Matthews, RSKERL	12/86

TABLE 1. Continued.

Research Activity	Contacts	Output Date
20. Indicator Selection Procedures HWLT Unsaturated Zone Monitoring (Task 225)	Dr. S. P. C. Rao, University of Florida Dr. Tom Short, RSKERL	04/86
21. Pilot Land Treatment Research Facility (Task 224)	Dr. Mickey Rowe, East Central Okla. John Matthews, RSKERL	09/87
22. Land Treatability Banning Evaluations for Selected Hazardous Wastes (Task 245)	Dr. Barbara Walton, ORNL Dr. R. C. Loehr, University of Texas John Matthews, RSKERL	09/87
23. Land Treatment of Wood Preserving Chemicals (Task 243)	Dr. Gary McGinnis, Mississippi State University John Matthews, RSKERL	01/86 01/87 01/88
24. Land Treatability of Petrochemical Waste Sludge (TA Project)*	Fred Pfeffer, RSKERL	06/83
25. Land Treatment of Oily Waste Lagoon Sludge (TA Project)	Fred Pfeffer, RSKERL	08/83
26. Toxicity Test Procedure for Land Treatment Demonstrations (Task 230)	John Matthews, RSKERL	09/85
27. Predictive Model for Land Treatability (Task 244)	Dr. Tom Short, RSKERL	09/85 09/87
28. Screening Program for Demonstrating HW Land Treatability (Task 230)	John Matthews, RSKERL	09/83 04/84 09/87
29. Fate and Effects of Toxaphene at HWLT Sites (Task 242)	Dr. Ron Sims, Utah State University John Matthews, RSKERL	12/86

*Technical Assistance Project

TABLE 2. HWLT research program outputs (U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory).

Project/Task	EPA Needs	Delivery Date/Key Outputs
1. Landfarming air emissions (210)	Support development of air standards for HWLT units.	Completed 06/84: Project summary/report PS*: EPA-600/52-84-108, July 1984 PR*: PB 84-20966, June 1984 "Laboratory Assessment of Potential Hydrocarbon Emissions from Land Treatment of Oil Sludges"
2. HWLT site selection (224)	Support development of guidance for HWLT unit site selection to facilitate implementation of Part 264 Permitting Regulations	Completed 06/84: Final report to OSW Internal report: "Site Selection Criteria for Hazardous Waste Land Treatment Facilities"
3. Land treatment technology development for hazardous wastes (214)	a. Information base of published literature pertaining to land treatment of hazardous waste.	a. Completed 06/84: Project summary/report PS: EPA-600/2-84-098, June 1984 PR: PB 84-195270, May 1984 "Annotated Literature References on Land Treatment of Hazardous Waste"

*PS - Project Summary; PR - Project Report
**Corvallis Environmental Research laboratory, U.S. EPA, Corvallis, Oregon.

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
	b. Peer conceived HWLT research plan.	b. HWLT research plan finalized 10/82; submitted to ORD headquarters
	c. Oversight peer panel for HWLT research program.	c. Peer panel established 08/81-05/84
4. a. Use of bioassays to evaluate impact of industrial waste land treatment (220)	Support development of RCRA Regulations for HWLT guidance documents for implementing such regulations.	Completed 08/84: Project summary/report PS: EPA-600/2-84-135, August 1984 PR: PB 84-232560, August 1984 "Use of Short-Term Bioassays to Evaluate Environmental Impact of Land Treatment of Hazardous Industrial Waste"
b. Use of bioassays to evaluate unsaturated zone monitoring procedure (226)	Evaluation of effectiveness of soil core vs. soil pore liquid-monitoring practices for detecting fast moving chemicals.	
5. Closure evaluation for petroleum residue land treatment sites (209)	Support regulations development for HWLT site closure requirements.	Completed 09/84: Project summary/report PS: EPA-600/2-84-162, October 1984 PR: PB 85-115822, October 1984 "Closure Evaluation for Petroleum Residue Land Treatment"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
6. Land treatment of petroleum refinery sludges (212)	Support development of RCRA regulations for HWLT units and guidance documents for implementation of such regulations.	Completed 11/84: Project summary/report PS: EPA-600/2-84-193, November 1984 PR: PB 85-148708 "Land Treatment of Petroleum Refinery Sludges"
7. a. HWLT microbial degradation kinetics (223)	a. Development of predictive models for use in determining amenability of hazardous wastes to land treatment.	Completed 12/84: Unpublished report/internal report a. Unpublished report "Kinetics of Hazardous Waste Biodegradation in Soil"
b. Summation of currently available land treatability screening procedures (228)	b. Support development of guidance document for conducting Part 264 land treatment demonstration.	b. Internal report submitted to OSW 05/84 "Summary of Currently Available Land Treatability Screening Procedures"
8. Screening terrestrial bioassay (237) [CERL project cofunded by RSKERL]	Support development of guidance for land treatment demonstration and operational and post-closure monitoring.	Completed 12/84: Final report to RSKERL Final report accepted by RSKERL 12/84 "A Harvester Ant Bioassay for Assessing Hazardous Chemical Waste Sites"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
9. a. Effects of land-applied industrial wastes on soil biota (215)	a. Support development of guidance for HWLT unit operational and post-closure monitoring.	Completed 12/84: Project summary/report PS: EPA/600/2-85-009 PR: PB 85-166353 "Land Treatment of an Oily Sludge--Degradation, Immobilization and Bioaccumulation"
b. High loading rate effects on degradation of oily sludge (231)	b. Support development of regulations for high intensity treatment units and guidance for unit operations.	
10. Evaluation of HWLT unit operational procedure (238)	Support development of HWLT site operation guidance documents.	Completed 04/85: 3 journal articles submitted for publication
11. Land treatment of ignitable and corrosive wastes (232)	Assessment of practice; support regulations development, if deemed necessary.	Scheduled completion 08/85: Project summary/report "Land treatment of Ignitable and Corrosive Wastes, EPA Code D001 and D002"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
12. Land treatment of tannery sludges (222)	Land treatability assessment; support delisting of tannery sludges.	Scheduled completion 08/85: Project summary/report "Field Evaluation and Investigation of Land Treatment of Tannery Sludges"
13. Landfarm closure study (211)	Support development of guidance for closing HWLT sites in an environmentally acceptable manner.	Scheduled completion 09/85: Project summary/report "Evaluation of Closure Techniques in Petroleum Refinery Land Treatment Sites
14. Volatilization of hazardous compounds at HWLT sites (234)	Evaluation of air emissions at HWLT sites and the proposed air sampling procedures; field verification of the HWLT unit emissions model developed by GCA/ Radian for OSW.	Scheduled completion 10/85: Project summary/report "Evaluation of Volatilization of Hazardous Compounds at HWLT Sites"
15. Screening test battery for determining land treatability (230)	Support development of guidance document for conducting land treatment demonstrations.	Scheduled completion 12/85: Project summary/report "Evaluation of a Screening Test Battery for Determining Land Treatability of Hazardous Wastes"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
16. Effectiveness of soil-core/soil-pore liquid monitoring procedures (227)	Evaluation of effectiveness of soil core versus soil pore liquid U.Z. monitoring procedures for detecting fast-moving chemicals beneath land treatment units; support development of U.Z. guidance documents.	Scheduled completion 12/85: Project summary/report "Effectiveness of Soil-Core/Soil-Pore Liquid Monitoring Procedures in Detecting Fast-Moving Chemicals"
17. HWLT conference (239)	Dissemination of state-of-the-art information pertaining to use of land treatmentf as a hazardous waste management alternative.	Scheduled completion 12/85: Conference proceedings Conference dates: April 16-18, 1985 Austin, Texas Published peer-reviewed proceedings 12/85
18. Evaluation of specified HWLT unsaturated zone monitoring protocol (233)	Statistical information pertaining to the number of unsaturated zone core samples required to provide reliable data; support development of guidance for implementing unsaturated zone monitoring requirements in Part 264 permitting regulations.	Scheduled completion 12/85: Final report Report will be submitted to EMSL, Las Vegas, EPA, for inclusion with other data being collected.

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
19. a. Effects of loading on organics degradation and migration (236)	a. Development of HWLT site operational guidance document for use by permit writers in implementing part 204 regulations.	a. Scheduled completion 12/85: Project summary/report "Effects of Rate and Loading Frequency on Degradation and Migration of Hazardous Constituents in Land Treatment Systems"
b. Evaluation of high-intensity land treatment (235)	b. Assessment of high intensity land treatment practice in the petroleum refinery industry; support regulations development, if deemed necessary.	b. Scheduled completion 05/85: Final report "Evaluation of High-Intensity Land Treatment Practices in the Petroleum Refining Industry"
c. Land treatability banning evaluations (244)	c. Development of land treatability information base for listed hazardous wastes to support the banning decision process required by the Hazardous and Solid Waste Amendments of 1984.	c. Scheduled completion 12/86: Project summary/report "Land Treatability Potential for Listed Hazardous Waste--Vol.I"
20. Indicator selection procedures for HWLT unsaturated zone monitoring (255)	Development of Technical Resource Document (TRD) on indicator procedures for selecting hazardous constituents for unsaturated zone monitoring at HWLT sites.	Scheduled completion 04/86: TRD "Hazardous Constituent Indicator Selection Procedures for HWLT Unsaturated Zone Monitoring"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
21. Pilot land treatment research facility (224)	Establishment and operation of a national land treatment research facility as a permitted location to conduct field verification research and short-term technical support studies to meet Program Office needs in developing, implementing, and/or modifying regulations pertaining to HWLT.	Scheduled completion 09/87: Final project report Individual reports will be submitted for specific studies conducted at the facility.
22. Land treatability banning evaluations for selected hazardous wastes (244)	Development of land treatability information base for listed hazardous wastes to support the banning decision process required by the Hazardous and Solid Waste Amendments of 1984.	Scheduled completion 09/87: Project summary report "Land Treatability Potential for Listed Hazardous Wastes--Vol.II"
23. Land treatment of wood preserving chemicals (243)	Evaluation of the efficacy of land treatment for pentachlorophenol and creosote containing sludges and contaminated soils from the wood preserving industry; response to line item in FY-85 budget.	Scheduled completion 01/88: Final report Interim report 01/86: "Characterization of Sludge and Contaminated Soils" Interim report 01/87: "Bench-Scale Land Treatability Studies"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
		Final report: "Land Treatability of Pentachlorophenol and Creosote Containing Sludges and Contaminated Soils from the Wood Preserving Industry"
24. Land treatability of petrochemical waste sludge	Technical Assistance (TA) project with Rohm and Haas Corp.	Completed 06/83: Final report submitted to Rohm and Haas Corp.
25. Land treatability of oily waste lagoon sludge	TA project with Oklahoma State Health Department (OSHD) and Sun Refinery, Tulsa, OK.	Completed 08/83: Final report submitted to Sun Refinery and OSHD. Presentation to Purdue Industrial Waste Conference 05/84.
26. Toxicity test procedures for land treatment demonstrations (230)	Support development of guidance documents for land treatment demonstrations, operational monitoring, and post-closure monitoring.	Development work completed 09/84; (In-house) QA/QC evaluation scheduled for completion 09/85 Presentations: SETAC 11/83 "Toxicity Reduction Screening Procedure for Determining Land Treatability of Hazardous Wastes"

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
		Presentations/Publications: ASTM 05/84 "A Toxicity Reduction Test System to Assist in Predicting Land Treatability of Hazardous Organic Wastes" International Microbial Toxicity Testing Symposium/Bulletin (05/85): "Interlaboratory Evaluation of Toxicity Test Procedures for Use in Land Treatability Screening"
27. Predictive model for land treatability (244, 245)	Support land treatment banning requirements in Solid and Hazardous Waste Amendments of 1984.	Scheduled completion initial development: (in-house) 09/85; verification 09/87. "Predictive Model for Use in Making Land Treatability Decisions" (09/85) "Verification of Predictive Model for Use in Making Land Treatability Decisions" (09/87)

TABLE 2. Continued.

Project/Task	EPA Needs	Delivery Date/Key Outputs
28. Screening program for demonstrating hazardous waste land treatability (230, 244)	Support development of RCRA guidance document for land treatment demonstrations as required in the Part 264 regulations.	Scheduled completion 09/87 (in-house): Final Protocol Draft #1 09/83 (reviewed in-house and extramurally): "Screening Program for Demonstrating Hazardous Waste Land Treatability" Draft #2 04/84 (11 extramural reviews): "Screening Program for Demonstrating Hazardous Waste Land Treatability" Draft #2 plus peer review comments submitted to OSW 06/84.
29. Fate and Effects of toxaphene at HWLT sites (242)	Evaluation of amenability of spent toxaphene cattle dipping waste to land treatment; regulations development.	Scheduled completion (in-house/Utah State) 12/86: Final report Report to OSW "Land Treatability Potential of Spent Toxaphone Cattle Dipping Waste"

The most pressing future direction envisioned for the HWLT Research Program is to assist OAQPS in developing air standards and to complete development of the land treatability model for use by OSW in land treatability decision making. Verification studies are to be initiated immediately following development of the model. Refinement of the model to include additional parameters of concern, i.e., volatilization, is also needed. Treatability studies to obtain kinetics and transport data also are to be initiated for those listed wastes that contain hazardous organic constituents which are not commonly found in land treated wastes or that have a complex matrix of hazardous constituents. Other areas in which future research activities will be emphasized are: (a) the impact of soil amendments and cooxidation processes on the transport and fate of land treated wastes; (b) bioaccumulation potentials of land treated waste constituents, especially organics; (c) use of on-site and/or in situ land treatment as remedial action procedures; and (d) field verification of land treatability protocols.

ENDNOTE

*Although the information presented in this paper is the result of activities funded wholly or in part by the United States Environmental Protection Agency (EPA), this paper has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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Canviro Consultants, Ltd., 1983. The Significance of Trace Substances in Petroleum Industry Sludges Disposed of on Land: A Literature Survey. PACE Report No. 83-2, Prepared for the Petroleum Association for Conservation of the Canadian Environment, Ottawa, Ontario, Canada, 172 pages.

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VOLATILE EMISSIONS FROM LAND TREATMENT SYSTEMS

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INTRODUCTION

The disposal of organic wastes, including refinery sludges, by land treatment has become increasingly important. In recent years, there has been an increasing interest in defining the presence and magnitude of volatile organic compounds (VOC) emissions from land treatment activities. Radian Corporation has completed two studies to assess air emissions from the land treatment of oily sludges. Results of a third study are currently being reviewed by the EPA prior to their release.

Some of the results of these studies are presented in this paper. The first program was a laboratory study jointly funded by the U.S. Environmental Protection Agency and the American Petroleum Institute (1). The second study was performed for the EPA at a commercial hazardous waste disposal facility (2). A refinery land treatment facility was the site of the third study, which was also performed under an EPA contract.

LABORATORY STUDIES

The laboratory studies were performed to characterize refinery sludges and to evaluate the effects of operating and process variables on the short-term VOC emission levels. Some characterization of land farm soils was also performed. Fifteen different refinery sludges and nine land farm soil samples were collected and tested. A laboratory apparatus was developed to simulate land treatment activities. A number of land treatment simulation experiments were performed with this apparatus. Emissions were measured during these simulations, and some of the potentially important parameters affecting these emissions were identified.

Sludge Properties

The sludge samples from the participating refineries came from a variety of sources within the plants. These sludges include: dissolved air flotation float, API separator sludge, biological oxidation sludge, emulsion from wastewater holding pond, jet filter clay, emulsion plant filter clay, and tank bottoms. These sludge samples were tested to determine the chemical composition, the volatility, and the volume of oil, water, and solids. The chemical composition was determined by gas chromatography/mass spectrometry (GC/MS), and the oil, water, and solids were estimated by centrifugation. The volatility was characterized through a stripping test developed in the study. For this stripping test, a small amount of the sludge sample (1 ml) was added to a volume of hydrocarbon-free water. The sludge-water mixture was then purged for four hours with ultra-pure nitrogen. The nitrogen stream from the purging apparatus was continually monitored for the hydrocarbon content. The average hydrocarbon concentration over the four-hour stripping period was used as a quantitative measure of the relative volatility of the sludges.

The results of the sludge characterization tests are summarized in Table 1. The reported volumes of oil, water, and solids in the sludges should be considered as estimates. There are obviously some limitations associated with centrifugation. In some cases, emulsions (or emulsified material) were present, and the interface between layers was somewhat difficult to accurately define. Additionally, water-soluble organic material and oil which is occluded in the "solids" phase are not isolated during centrifugation. The apparent oil content of the sludges varied considerably from 10% (SL-18) to 94% (SI). The amounts of water and solids also varied widely.

The results of the sludge volatility tests are also presented in Table 1, as are the total concentrations of all compounds identified in the GC/MS analyses of the sludges. In general, the sludges having the higher concentrations of identified volatile compounds also appear to be the most volatile, as indicated by the results of the volatility tests.

The results of the GC/MS analyses of the sludges are shown in Table 2. The individual concentrations of selected compounds are included. The C_7 to C_9 aromatic compounds appear to dominate the volatile fraction of most of the sludges.

Land Treatment Simulation

Experimental Design. A parametric study was designed to evaluate the effects of five parameters on the short-term (0.5–8 hours after sludge application) emissions of VOC. These parameters and their ranges were: sludge volatility (low, medium, high), sludge loading (0.05–2.0 lb oil/square foot of soil), soil types (sand, silt, clay), soil moisture (5, 10, 15, 20, 25 wt% moisture), and air relative humidity (30, 50, 70%).

Experimental Equipment. The laboratory land treatment simulation device is shown schematically in Figure 1. Air was drawn by an induced draft into a duct, through a conditioning section, across a soil surface, and out through a

TABLE 1. Characterization tests results for refinery sludges.

Sludge ID#	Centrifugation Test (vol %) H_2O	Solids	Oil	GC/MS[a] (ug/gm)	Volatility Test[b] (ppm/ml)
S-1	0	6	94	347,700	14,260
S-2	50	40	10	36	217
S-3	79	15	6	277,000	263,000
SL-11	25	12.5	62.5	6,103	821
SL-12	40	25	35	685	71
SL-13	65	15	20	2,914	124
SL-15	---	100	---	2,796	268[c]
SL-16	---	100	---	3,162	136[c]
SL-17	80	7.5	12.5	1,314	71
SL-18	5	85	10	80	5.1
SL-19	---	100	---	10,536	191[c]

[a] Values are the sum of the concentrations of all identified compounds.

[b] Average hydocarbon concentration in the stripping gas over a 4-hour period, normalized to a sludge sample size of 1000 ul (1 ml).

[c] Values are ppm/gm.

blower. The duct in the conditioning and measurement section was 4 inches high and 12 inches wide. The incoming air was heated by several resistance heaters in a 3-foot section of the duct. The air temperature was automatically controlled with the controller thermocouple placed in the air stream just upstream of the soil chamber.

Moisture was added to the air stream from water contained in a heated pot. Power to this unit was manually adjusted to obtain the desired humidity. The amount of water in the pot was maintained at a relatively constant level by continually adding water with a peristaltic pump. The humidity was monitored just upstream of the soil chamber using a Versala Model HMP-14A humidity sensor. The soil was maintained at a slightly elevated temperature with a buried heater and automatic controller.

The removable soil boxes or chambers were 12 inches square with a depth of 4 to 12 inches. They were constructed of plexiglas and coupled to the duct with flexible plastic sheeting. When placed in the system, the box rested on an ana-

TABLE 2. Selected hydrogen concentration in sludges (Concentrations are in ug/gm as measured by GC/MS[a]).

Compound	S-1	S-2	S-3	SL-11	SL-12	SL-13	SL-14	SL-15	SL-16	SL-17	SL-18	SL-19
Benzene	1,800	ND	1,400	540	32	18	5	14	20	160	38	250
Toluene	9,300	0.02	5,600	1,700	58	98	14	ND	ND	150	36	2,200
m/p-Xylene	23,000	1.2	15,000	700	58	110	30	24	350	40	ND	1,400
o-Xylene	42,000	0.55	32,000	330	28	50	16	11	170	17	ND	510
C_3-Benzene	222,000	7.9	160,000	1,100	150	400	160	1,300	1,100	76	ND	2,800
C_3-Benzene	NR	NR	NR	890	120	400	140	620	900	60	ND	2,100
Naphthalene	NR	NR	NR	230	34	350	64	ND	50	500	ND	400
Anthr./Phen.	NR	NR	NR	150	20	1,100	92	20	210	120	ND	150
C_9-H.C. (alkane)	NR	NR	NR	130	30	14	36	160	8	13	ND	180
C_{12}-H.C. (alkane)	NR	NR	NR	140	57	210	120	410	200	44	ND	230
C_{17}-H.C. (alkane)	NR	NR	NR	84	72	84	68	120	84	60	6	130
C_{17}-H.C. (alkane) (pristane)	NR	NR	NR	66	72	24	68	99	84	34	6	78
C_{19}-H.C.	NR	NR	NR	31	26	40	28	18	54	14	ND	70
C_{20}-H.C.	NR	NR	NR	2	NM	16	14	ND	32	26	ND	38

[a] Light aromatics quantitated based on d_8-toluene. Naphthalene, anthr./phen., and alkanes based on d_{10}-anthracene.

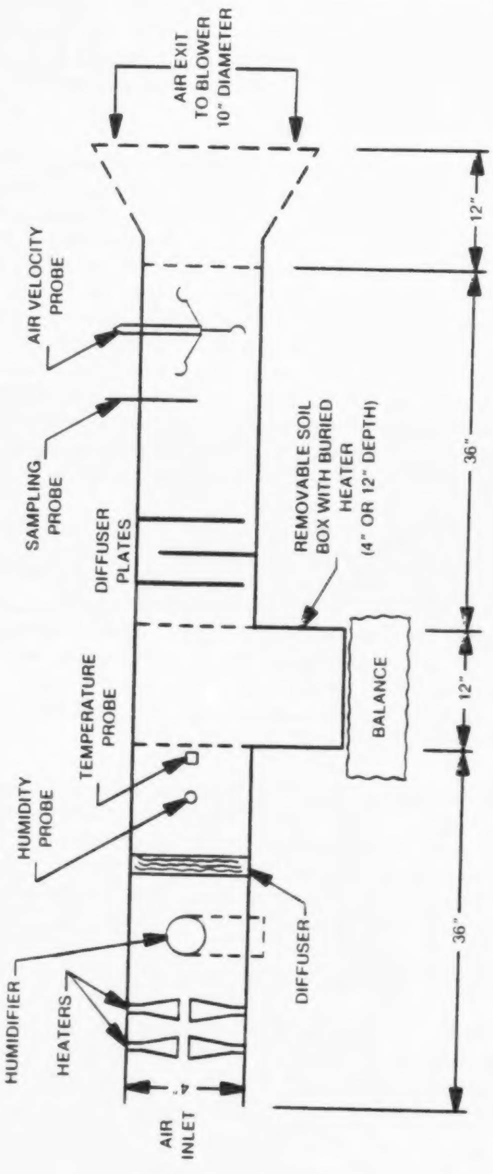
AIR EXIT
TO BLOWER
10" DIAMETER
AIR VELOCITY
PROBE
SAMPLING
PROBE
DIFFUSER
PLATES
REMOVABLE SOIL
BOX WITH BURIED
HEATER
(4" OR 12" DEPTH)
TEMPERATURE
PROBE
HUMIDITY
PROBE
BALANCE
HUMIDIFIER
HEATERS
DIFFUSER
AIR
INLET
4"
12"
36"
12"
36"

FIGURE 1. Laboratory land treatment simulation apparatus.

lytical balance capable of measuring to the nearest 0.01 pound. The air velocity in the duct was monitored continuously with a Met 1, Inc. Model 010 anemometer. A Byron Instruments Model 401 Total Hydrocarbon Analyzer was used to monitor the VOC concentration in the air downstream of the soil chamber. A microcomputer-based data acquisition system was used with the analyzer to record and process the analyzer output signals.

Experimental Procedure. The basic experimental procedure was quite similar for all of the laboratory simulation tests. Prior to starting an experimental run, the moisture content of the soil to be used was adjusted to the desired level by adding a known amount of water to a previously-dried quantity of soil. The soil was then placed in a soil chamber, and a soil heater was installed. The soil chamber was placed in position in the simulation apparatus. The air velocity was set at 3 mph, the air temperature was set at 90°F, and the soil temperature was adjusted to 90°F. When all conditions were constant at the desired values, the top of the soil chamber was opened. A weighed amount of sludge was spread evenly over the surface of the soil in the soil chamber. The cover was then installed back on the chamber. The experiment was then continued for up to eight hours, and all the test parameters were monitored during the course of the experiment. In a few of the experiments, the soil was manually tilled after several hours to determine the effect of tilling on the level of emissions.

In addition to the continuous monitoring of total VOC, some grab samples were taken for analysis by gas chromatography (GC). The samples were collected in stainless steel canisters of approxiately 2.7 L volume. The canisters were equipped with a shut-off valve and a vacuum flow regulator. Integrated samples of the VOC-laden air were taken over periods of 30–60 minutes. The samples were analyzed on a Varian Model 3700 gas chromatograph. Sample analysis involved cryogenic concentration, gas chromatographic separation, detection by multiple detectors, and data evaluation by a dedicated microcomputer. This system has been described elsewhere (1).

Predictive Model. Thibodeaux and Hwang (4) have proposed a mathematical model for the prediction of volatile compound emission rates from land treatment operations. The model is applicable for single compounds after the applied sludge has been incorporated into the soil. The model is shown in Table 3. Some data were collected to allow a very limited comparison of the measured emission rates to those predicted with the Thibodeaux-Hwang model.

Results of Land Treatment Simulation Experiments

Measured Emissions. The results of the experiments are briefly summarized in Table 4. The total cumulative VOC emissions at four hours after sludge application were selected for correlation with the selected experimental parameters. The four-hour data were chosen because there were more data available than at the longer periods.

TABLE 3. Proposed mathematical model.

Model: Thibodeaux-Hwang (4)
Disposal Method: Land treatment
Type of Model: Predictive
Basis: Emission rate is controlled by diffusion of vapor through the air-filled pores of the land treated soil.

Form:

$$q_i = \frac{D_{ei}C_{ig}}{\left[h_s^2 + \frac{2\,D_{ei}\,t\,A\,(h_p - h_s)C_{ig}}{M_{io}}\right]^{1/2}}$$

and

$$C_{ig} = \left[\frac{H_c}{1 + H_c\left(\frac{D_{ei}\,Z_o}{D_{wi}A_s\,f(\bar{y})}\right)}\right]C_{io}$$

where:

q_i = flux of component i from the soil surface, g/cm^2-sec
D_{ei} = effective diffusivity of component i in the air-filled soil pore spaces, cm^2/s
C_{ig} = effective wet zone pore space concentration of component i, g/cm^3
h_s = depth of subsurface injection (if applicable), cm
h_p = depth of soil contaminated or wetted with land treated waste, cm
t = time after application, sec
A = surface area over which waste is applied, cm^2
M_{io} = initial mass of component i incorporated into the zone (h_p-h_s), g
H_c = Henry's-law constant in concentration form, cm^3 oil/cm^3 air
Z_o = oil layer diffusion length, cm
D_{wi} = effective diffusivity of species i in the oil, cm$_2$/s
A_s = interfacial area per unit volume of soil for the oily waste, cm$_2$/cm$_3$
$f(\bar{y})$ = $\bar{y}$ (h_p-$\bar{y}$), accounts for the lengthening dry zone
$\bar{y}$ = height of wetted soil remaining after partial drying, cm

TABLE 4. Summary of results of laboratory land treatment emissions study.

Elapsed Time After Sludge Application, Hr	Measured Emission Rates for Elapsed Time Period	
	Lb VOC/ft^2	% of Applied Oil
0.5	0.0 - 0.059	0.0 - 4.0
2.0	0.0 - 0.036	0.0 - 4.2
4.0	0.0 - 0.043	0.0 - 6.0
7.0	0.0 - 0.038	0.0 - 9.2
8.0	0.0 - 0.030	0.0 - 9.9

Multiple regression techniques were used to evaluate a number of mathematical expressions relating the emission levels to various parameters. Only three of the parameters studied appeared to have a significant effect on the emission levels. These were: sludge volatility (V), sludge loading (L), and air humidity (H).

The model containing these parameters which appears to be simple and most descriptive is:

$$E = aVL(100H\text{-}H_2)^d + g$$

where, E = total emissions at four hours (lb/ft^2), V = sludge volatility (measured during four-hour stripping test, ppm/ml), L = sludge oil loading on soil, (lb oil/ft^2), H = relative humidity, (%), $a = 6.94 \times 10^{-14}$, $d = 2.609$, and $g = 4.1 \times 10^{-5}$. The correlation coefficient for this model is 0.939. The predicted accuracy of this model is illustrated in Figure 2. An alternate response variable E2 (the emission level at seven hours after spreading) was also tested with the preferred model. It showed a correlation coefficient of 0.97, indicating that conclusions developed with four-hour data were also applicable to the seven-hour data.

The effect of elapsed time (after sludge application) on the VOC emission rates was quite dramatic. The form of the hydrocarbon concentration-elapsed time curve is generally quite similar for most tests. This is illustrated in Figure 3 which is the concentration-time curve for Run No. 41. Immediately after the application of the sludge, the concentration of VOC in the air from the soil chamber rose to a peak detected value of 24 ppmv. The concentration then declined in an exponential manner over the next four hours to levels in the range of 2 ppmv. Approximately 1.8% of the applied oil was vaporized in this four-hour period.

The fraction of applied oil which was vaporized during the tests ranged from 0 to 9.8% at eight hours after sludge application. The vaporization behavior is

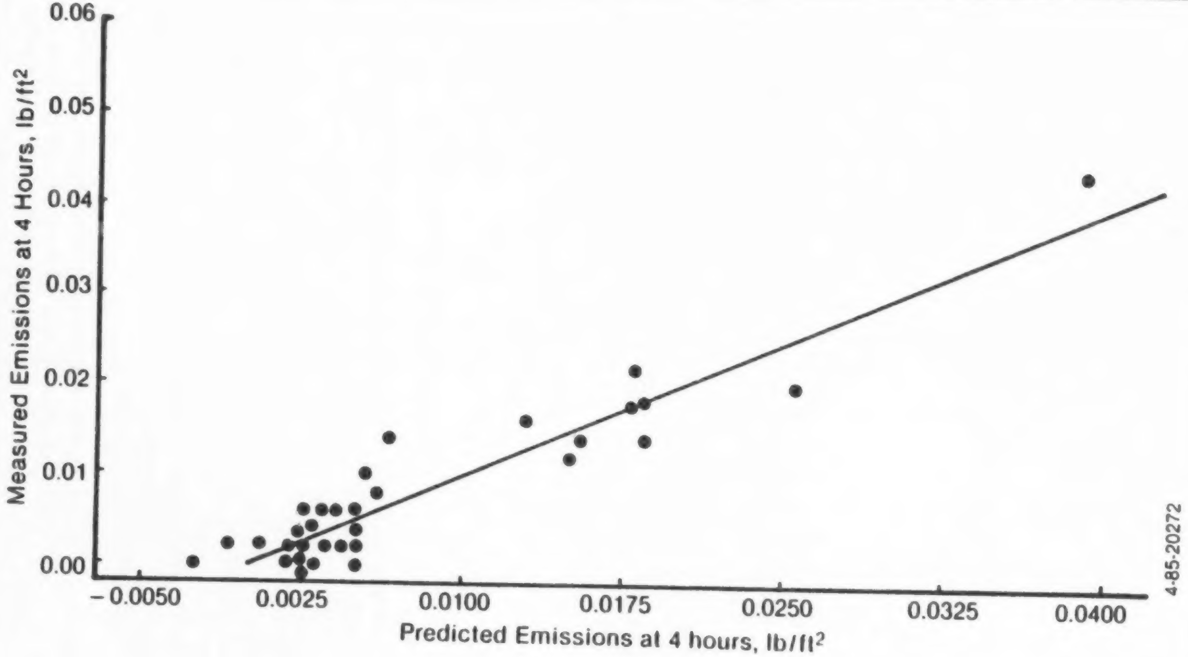

FIGURE 2. Comparison of experimental and predicted values of E, emission levels at four hours after spreading.

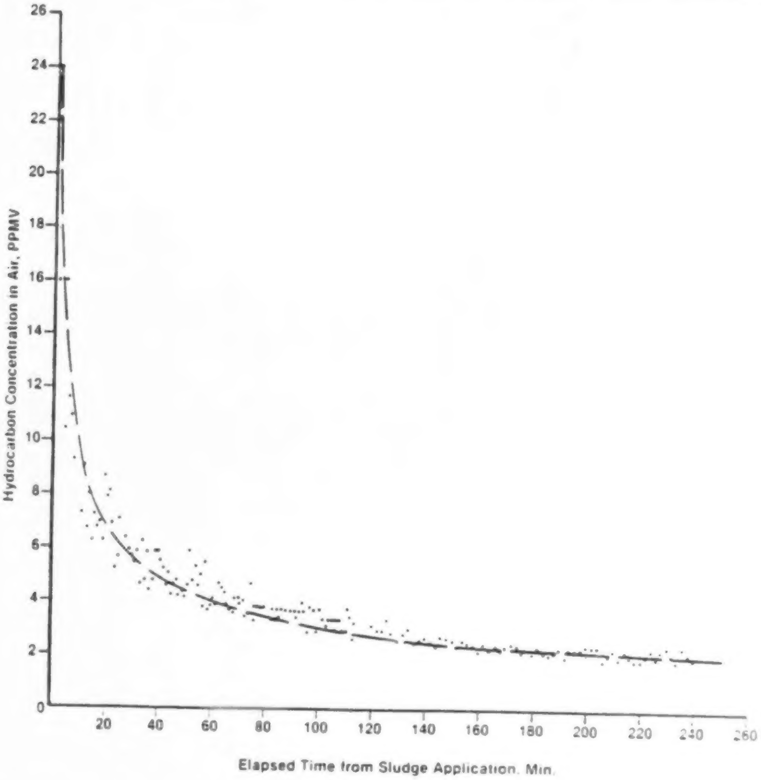

FIGURE 3. Hydrocarbon concentration in air during run 12 (0.6 lb of SL - 11 on soil D-1).

summarized in Table 5. The overall average percentage of vaporized oil was 2.0% and 3.4% at four and seven hours, respectively, after sludge application.

Detailed GC analyses were performed on air samples collected during several runs. Some of the results are shown in Table 6. As may be anticipated, the results indicate that the more volatile components of the sludge are emitted into the air. The more volatile compounds are generally present in the air at relatively higher concentrations than found in the sludge.

Comparison of Measured and Predicted Emission Rates. In one experimental run (No. 29), a sample of the air from the soil chamber was collected over a one-hour period, starting four hours after sludge application. At this point, the sludge had soaked into the soil, and the Thibodeaux-Hwang model was appli-

TABLE 5. Vaporization of oily sludge.

Sludge	Amount of Oil Sludge Vaporized, % of Applied Oil [a]						Oil Vaporized During Four-Hour Stripping Test, % of Oil in Sludge
	Four Hours After Application			Six Hours After Application			
	Average	Maximum	Minimum	Average	Maximum	Minimum	
SL-11	3.3	6.0	0.6	4.1	8.4	0.6	46.6
SL-12	0.5	1.4	0.06	0.9	1.8	0.15	6.0
SL-13	1.9	4.1	0.15	4.0	8.4	0.4	18.4
SL-14	1.8	5.9	0.0	3.6	9.2	0.0	12.2
	2.0			3.4			

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[a] Applied oil amount estimated from results of centrifugation tests.

TABLE 6. Composition of air from soil chamber during tests with sludge SL-14.

	Concentration in Sludge		Run 29 SL-14 on D-1 Concentration in Air[a] ppbv-C	Run 29 SL-14 on D-1 Concentration in Air[a] ppbv-C	Run 39 SL-14 on D-1 Concentration in Air[a] ppbv-C	Run 42 SL-14 on D-1 Concentration in Air[a] ppbv-C
	ug/gm	Weight Percent				
Benzene	5	0.6	204	72	21	53
Toluene	14	1.8	166	200	72	94
m/p-Xylene	30	3.8	51	73	30	64
o-Xylene	16	2.0	–	–	10	13
C_3-Benzene	160	20.4				
C_3-Benzene	140	17.8	363	39	34	94
Naphthalene	64	8.1	185	52	–	–
Anthr./Phen.	92	11.7	–	–	–	–
C_9-H.C. (alkane)	36	4.6	19	–	–	53
C_{12}-H.C. (alkane)	120	15.2	–	–	–	–
C_{17}-H.C. (alkane)						
C_{17}-H.C. (alkane) (pristane)	68	8.6	–	–	–	–
C_{19}-H.C.	28	3.6	–	–	–	–
C_{20}-H.C.	14	1.8	–	–	–	–
	787					
Sampling Time Period:			Collected for 60 minutes at start of run	Collected for 60 minutes at 4 hours after start of run	Collected for 1 hour at start of run	Collected for 30 minutes at start of run

[a] Dashed line indicates that the compound was not detected in the air sample.

cable. The average experimental emission rates were compared to the emission rates calculated with the Thibodeaux-Hwang model. The experimental and calculated rates for four selected compounds are summarized in Table 7. Relatively good agreement was obtained for three of the four selected compounds. A considerable difference was observed between the calculated and measured emission rates for m/p-xylene.

TABLE 7. Comparison of predicted and measured emission rates of individual components during experiment run 29.

Compound	Emission Rate, gr/cm^2-sec Experimental	Predicted
Benzene	1.77×10^{-9}	1.26×10^{-9}
Toluene	4.87×10^{-9}	3.66×10^{-9}
m/p-Xylene	1.81×10^{-9}	9.02×10^{-9}
Naphthalene	1.18×10^{-9}	2.45×10^{-9}

FIELD STUDIES AT A WASTE TREATMENT FACILITY

In 1983 Radian performed air emissions studies at a commercial waste disposal operation located in the Gulf Coast area. The objective of the EPA-sponsored program was to develop and verify techniques for determining air emissions from treatment, storage, and disposal operations at hazardous waste disposal facilities. The waste disposal facility included a land treatment area, and VOC emissions were measured from this area. The results are summarized below.

Site Description

The land farm at this site is a single ten-acre plot. Liquid waste is received by tank truck and discharged through flexible hose onto the soil surface. It is then spread with a toothed harrow (teeth up). The dimensions of the application area observed during this field test were nominally 100 feet x 60 feet. The oil content of waste applied to this area was estimated to be 20% by weight. After the initial application and spreading, the waste was tilled for a one- to two-hour period on a daily basis.

Approach

Air emissions were measured using two different sampling approaches; concentration profile and emission isolation flux chamber.

Concentration Profile (C-P) Technique. The C-P technique was developed by L. J. Thibodeaux and coworkers at the University of Arkansas under a U.S. EPA contract (5). The C-P technique, as developed by Thibodeaux, has been used to estimate emission rates of volatile species from wastewater treatment ponds (5) and more recently, from land areas (6). The C-P approach is an indirect sampling technique predicated upon experimental measurements of wind velocity, volatile specie(s) concentration, and temperature profiles in the boundary layer above the waste body. Details of this technique can be found elsewhere (7).

Emission Isolation Flux Chamber. The emission isolation flux chamber was used to make direct emission measurements from the surface of the land treatment area. A diagram of the flux chamber apparatus used for measuring emissions from the land treatment area is shown in Figure 4. The sampling equipment consisted of a stainless steel/acrylic chamber with impeller, ultra-high purity sweep air, rotameter for measuring air flow into the chamber, and a sampling manifold for monitoring and/or collection of the species of interest. During the emission measurement, clean, dry, ultra-pure air is added to the chamber at a fixed and controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the specie(s) of interest is measured at the exit of the chamber. The emission rate of the specie(s) can then be calculated. Additional details of the experimental technique and calculational methods can be found elsewhere (8).

Concentrations of total hydrocarbons in the chamber outlet gas stream were continuously monitored using portable flame ionization detector (FID), and/or photoionization detector (PID)-based analyzers. In addition, samples were collected for subsequent gas chromatographic (GC) analysis using both gas-tight syringes (on-site analyses) and evacuated stainless steel canisters (off-site analyses).

Sampling Procedures. Three C-P runs were made during a twenty-four hour period at the land farm. Flux chamber sampling was performed over a four-day period immediately following the application of sludge. The area of application was divided into six segments or grid points of equal size. One location was selected as a control point, and replicate flux chamber sampling was regularly performed at this point. Periodic sampling was performed at several of the other grid points.

Measured Air Emission Rates

The emission rates of several individual volatile organic compounds, as well as those of classes of compounds, were estimated from the results of the concentration-profile and flux chamber measurements. Some of these results are

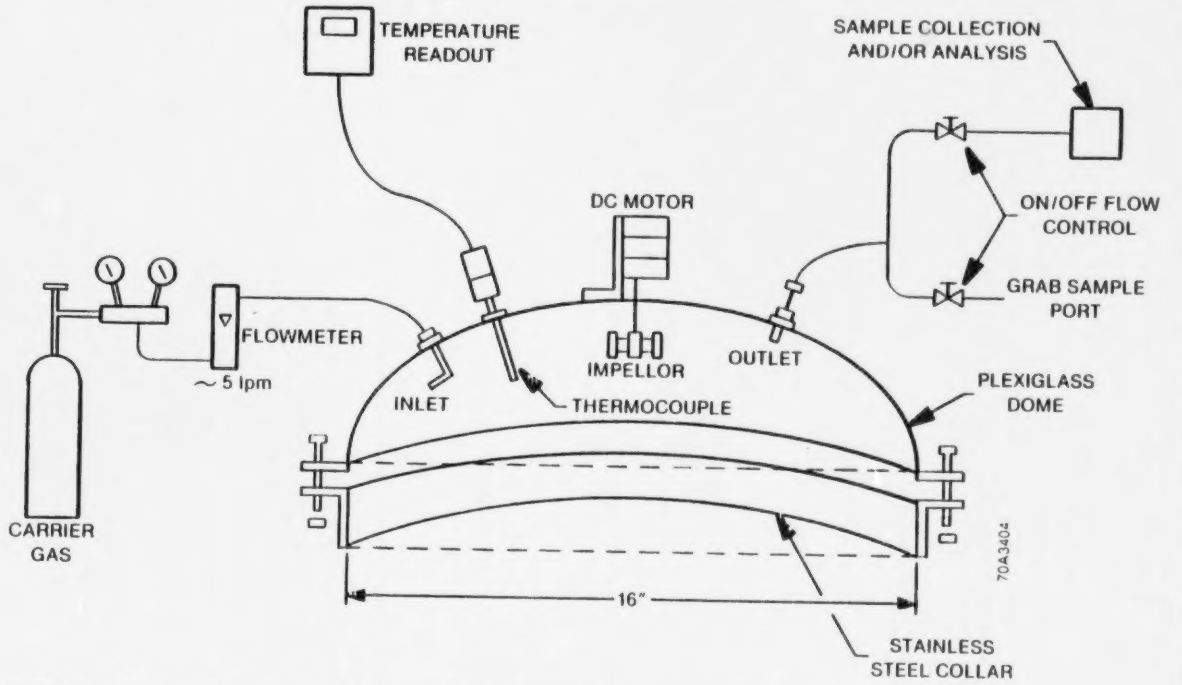
TEMPERATURE READOUT
SAMPLE COLLECTION AND/OR ANALYSIS
DC MOTOR
ON/OFF FLOW CONTROL
GRAB SAMPLE PORT
FLOWMETER
~ 5 lpm
IMPELLOR
OUTLET
INLET
THERMOCOUPLE
PLEXIGLASS DOME
CARRIER GAS
70A3404
16″
STAINLESS STEEL COLLAR

FIGURE 4. Cutaway side view of emission isolation flux chamber and sampling apparatus.

summarized in Table 8. The emission rates should decline with time after the initial sludge application, provided that no additional sludge is applied and the land treatment area is generally undisturbed. Although the land treatment area was raked/tilled on a daily basis, an overall general downward trend in the emission rates was observed. The measured rates at Grid Point 5 are consistently higher than those measured at Grid Point 4. The method of spreading the sludge at this site appeared to result in a somewhat uneven application over the land treatment area. The uneven application may have been at least partially responsible for the difference in emission rates measured at the different locations.

Predicted Emission Rates

The Thibodeaux-Hwang model was used to predict the emission rates of selected compounds and compound classes from the land treatment area. The rates were calculated at six different times. These times correspond to the times at which emission rates were measured by either the C-P or flux chamber methods. Some of the predicted rates are included in Table 8. Although the predicted rates were generally higher than the measured rates, the predicted rates compare reasonably well to many of the measured rates of the individual compounds. Agreement was poor, however, between the measured and predicted emission rates of the compound groups or classes. In all of these latter cases, the predicted emission rates were much higher than the measured rates. The differences are probably a result of having to use composite properties in the mathematical model when calculating the emission rates of the compound classes.

The predicted emission rates presented in Table 8 were calculated without considering the effect of tilling. In the period immediately following tilling, the emission rates can be expected to increase. Soil containing oil and volatile compounds is brought to the surface replacing soil which has been "dried" to some extent. Figure 5 shows the predicted and measured emission rates for cyclohexane as a function of the time elapsed since sludge application. The predicted rate curve shown in this figure was calculated without considering the effect of tilling.

The effect of tilling on the calculated emission rates of cyclohexane is shown in Figure 6. Frequent tilling appears to enhance the short-term emission rates, but probably does not have as great an impact on the total long-term emissions from a land treatment site.

FIELD STUDIES AT A REFINERY LAND TREATMENT SITE

Under contract by the EPA, Radian has recently completed a field study at a petroleum refinery land treatment site. The results of this study have not been completed, so details cannot be revealed at this time. As part of this study, however, oily sludge was applied on the surface of a small test plot in the land treatment area. The sludge was immediately tilled into the soil, and emission measurements were initiated. The plot was approximately 0.1 acre in area. Emission rates were measured with emission isolation flux chambers. Emission measure-

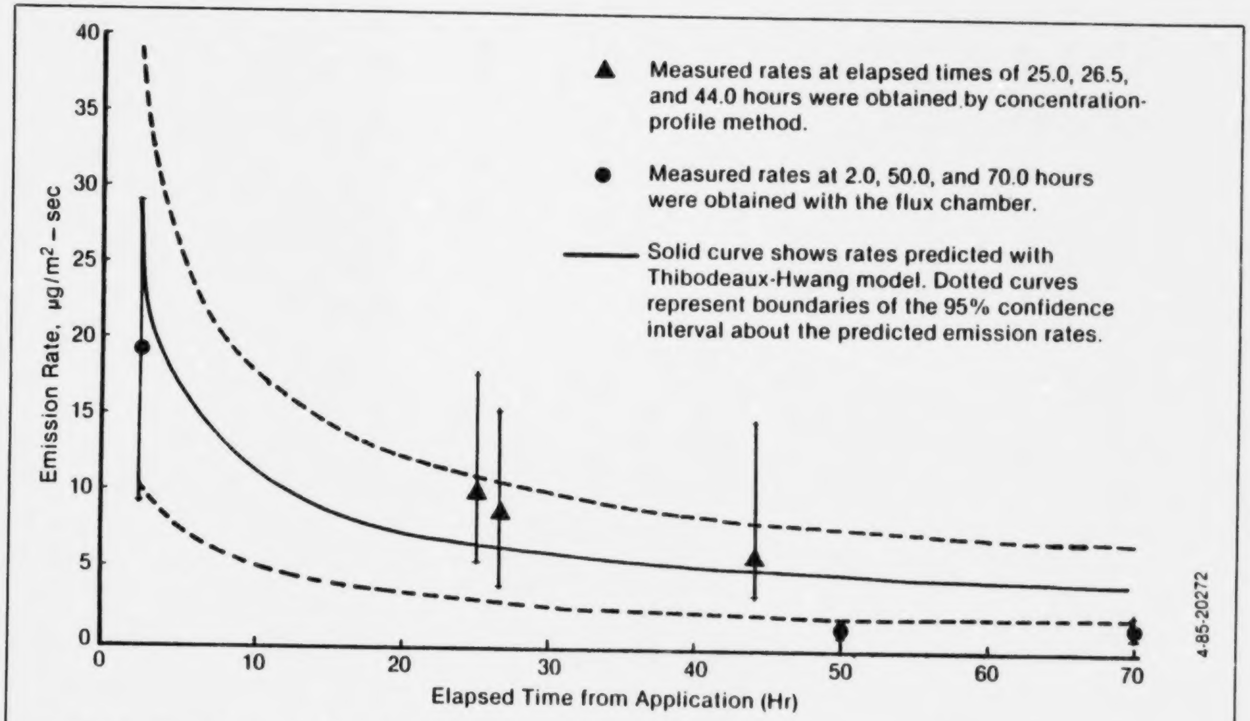

FIGURE 5. Comparison of predicted and measured emission rates ($\mu g/m^2$ - sec) of cyclohexane from land treatment area.

TABLE 8. Measured and predicted emission rates of selected compounds from landtreatment area, hazardous waste disposal facility.

Compound or Compound Class	Approximate Elapsed Time from Sludge Application, Hr	Measured Emission Rates: Measurement Method	Measured Emission Rates: Measured Grid Point	Measured Emission Rates: Emission Rate, ug/m^2-sec	Predicted Emission Rates, ug/m^2-sec
Methylcyclohexane	2.0	FC	Control	52.8 (27.6,87.7)	116 (48.4, 189)
	25.0	CP	–	40.2 (23.5,676)	33.0 (15.1,52.7)
	26.5	CP	–	35.0 (16.1,58.3)	32.1 (17.2,49.0)
	44.0	CP	–	25.9 (11.6,62.7)	24.9 (13.3,40.9)
	50.0	FC	4	3.47 (1.86,5.85)	23.3 (9.43,37.7)
	70.0	FC	5	4.93 (2.52,7.73)	19.7 (9.87,31.0)
Benzene	2.0	FC	Control	27.9 (13.9,43.3)	582 (2.31,936)
	25.0	CP	–	13.7 (617,23.8)	165 (78.0,262)
	26.5	CP	–	11.6 (5.03,20.0)	124 (64.0,2.65)
	44.0	CP	–	5.81 (2.56,14.0)	124 (56.4,192)
	50.0	FC	4	0.849 (0.440,1.36)	116 (50.4,187)
	70.0	FC	5	1.13 (0.53,1.76)	98.3 (51.2,150)
Toluene	2.0	FC	Control	74.2 (38.0,118)	61.0 (28.4,90.7)
	25.0	CP	–	70.6 (36.6,119)	17.3 (7.27,27.8)
	26.5	CP	–	53.2 (23.6,92.6)	16.8 (6.68,26.1)
	44.0	CP	–	31.6 (15.3,85.0)	13.0 (6.39,21.8)
	50.0	FC	4	2.86 (1.31,4.71)	12.2 (5.57,18.9)
	70.0	FC	5	4.71 (2.29,7.34)	10.3 (5.14,16.0)

TABLE 8. Continued.

Compound or Compound Class	Approximate Elapsed Time from Sludge Application, Hr	Measured Emission Rates			Predicted Emission Rates, ug/m²-sec
		Measurement Method[a]	Measured Grid Point	Emission Rate, ug/m²-sec	
Paraffins	2.0	FC	Control	391 (186,630)	21200 (102000,36400)
	25.0	CP	–	428 (249,696)	6000 (2960,9170)
	26.5	CP	–	351 (143,632)	5830 (2630,9500)
	44.0	CP	–	339 (188,816)	4520 (2200,6900)
	50.0	FC	4	30.0 (15.4,45.3)	4240 (2060,6680)
	70.0	FC	5	48.4 (23.4,74.8)	3580 (1280,5700)
Total Aromatics	2.0	FC	Control	244 (123,382)	15300 (7070,26400)
	25.0	CP	–	570 (350,905)	4330 (2000,7200)
	26.5	CP	–	436 (183,736)	4210 (1980,7100)
	44.0	CP	–	439 (182,1240)	3260 (1400,5490)
	50.0	FC	4	21.0 (10.9,34.5)	3060 (1250,4580)
	70.0	FC	5	45.9 (22.4,73.6)	2590 (990,3850)
Total NMHC	2.0	FC	Control	725 (377,1120)	47400 (16800,71700)
	25.0	CP	–	1250 (698,2290)	13400 (5710,22800)
	26.5	CP	–	963 (382,1720)	13000 (5560,20900)
	44.0	CP	–	1000 (1460,2020)	10100 (4710,16200)
	50.0	FC	4	60.8 (36.3,89.3)	9480 (3500,14500)
	70.0	FC	5	112 (53.9,172)	8010 (3950,13500)

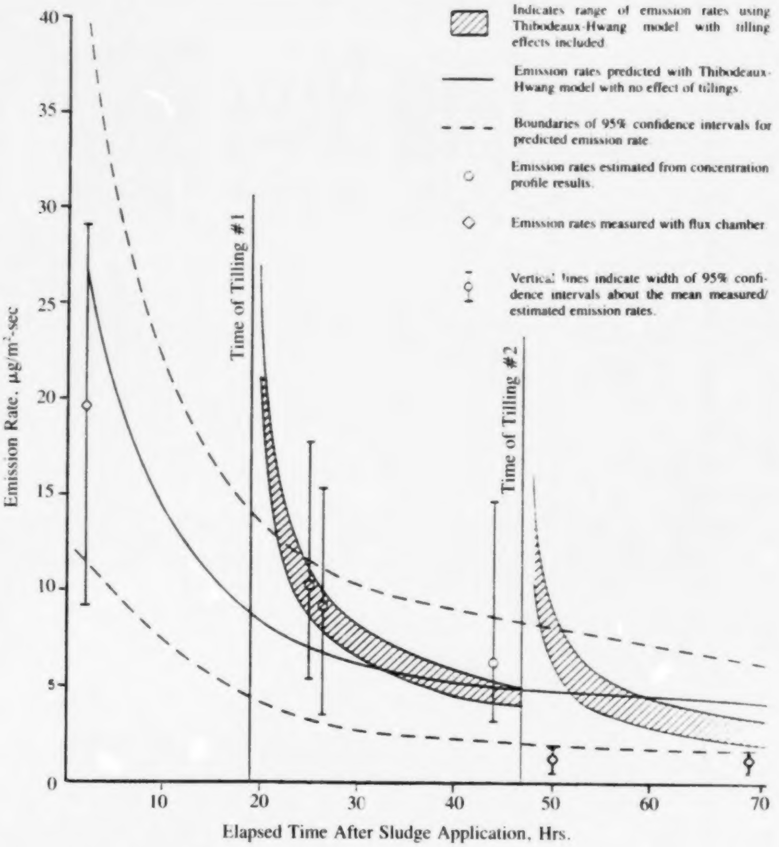

FIGURE 6. Estimated effect of tilling on the emission rate of cyclohexane from the land treatment area.

ments were performed during three, four-day test periods over a total interval of approximately five weeks. Parameters that were measured during the test period included: oil content of the soil, moisture content of the soil, physical properties of the soil (particle size, bulk density, particle density), microbe content of the soil, air and oil temperatures, air humidity, wind speed and direction, and CO_2 evolution rate.

The test plot was divided into 21 segments, and emission rate measurements were made each day at several randomly selected segments. Emission measurements were also made at a background plot adjacent to the application plot. No sludge was applied on the background plot.

The emission rate patterns determined at this test plot are similar in many respects to those found in previous laboratory and field studies. The cumulative emissions were estimated from the field measurements, and the shape of this curve is shown in Figure 7. The emission rates between measurement periods were interpolated from the actual measurement results. The curve shows the typical higher emission rates occurring during the period immediately following application. The emission rates then begin to decline exponentially with time. The test plot was tilled periodically over the test period. The emission rates generally increased significantly for a short period of time immediately following the tilling. A typical pattern is presented in Figure 8, which shows the measured emission rates from both the test and background plots before and after tilling. No further data are yet available from these experiments. The results are currently being reviewed, however. Publication of the results are expected in the near future.

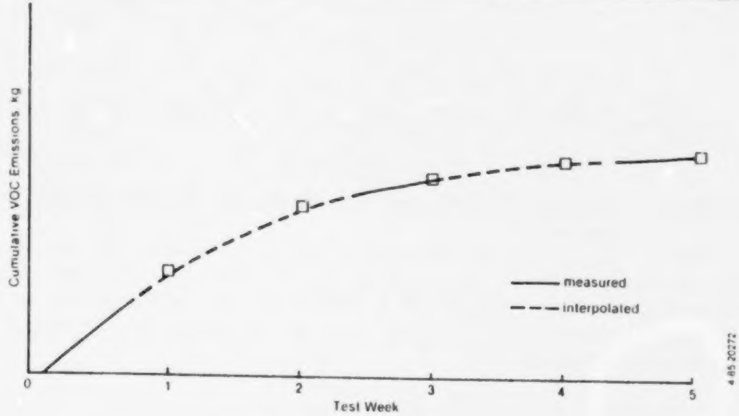

FIGURE 7. Cumulative estimated VOC emissions from test plot at refinery land treatment site.

CONCLUSIONS

The results obtained in recent land treatment studies support the following conclusions: the emission rates reach their maximum in a relatively short time after surface application of a volatile sludge; the most significant parameters affecting the emission rate from surface applications of sludge are the loading and the sludge volatility; the Thibodeaux-Hwang emission model appears to agree reasonably well with the measured rates for some selected compounds; the Thibodeaux-Hwang emission model has not been generally applicable to multicomponent mixtures, probably because of the uncertainty in defining accurate

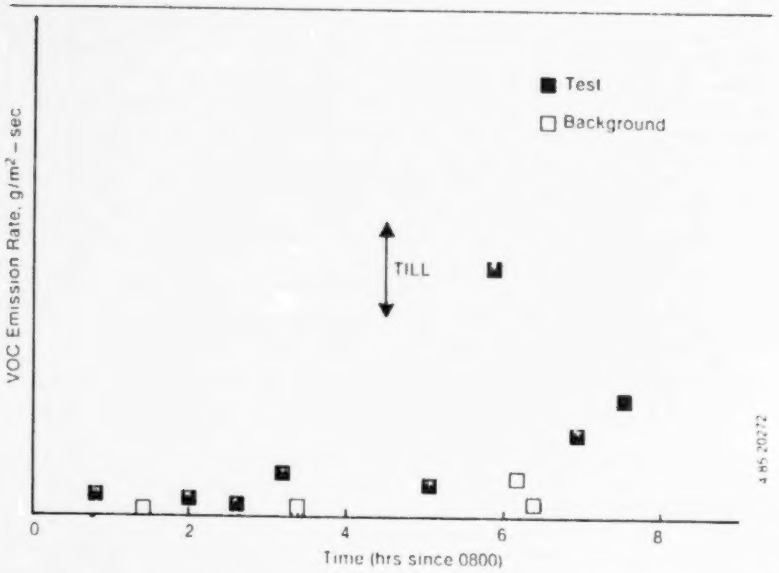

FIGURE 8. Measured VOC emission rates for October 24, 1984, refinery land treatment test plot.

multicomponent parameters for use in the model; during land treatment, a significant fraction of the applied VOC is emitted from the surface application of oily sludge; tilling causes a significant, short-term increase in the VOC emission rate from land treatment sites.

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DISCLAIMER

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LAND APPLYING SALINE INDUSTRIAL WASTE ACTIVATED SLUDGE

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INTRODUCTION

The program discussed in this paper has its roots in 1976 when there was contemplation of the optimum method of disposing of waste activated sludge from our biological waste treatment system. After considering many options, land application was selected because of its low cost and probable feasibility. There was a concern for the high dissolved salts in the sludge and their ultimate effects on both soil and crops grown on the land. At some time, or at some ultimate loading rate, certain negative effects could occur. An experimental design was developed, and a five year test program took place which involved a relatively small three acre area where conditions were rigorously controlled, while the full-scale study area was about 200 acres at that time. This paper will address some of the details of our testing program, the experimental design, supplementary testing on the full-scale areas, and some results and corrective measures. How all this relates to hazardous waste deposition on land will depend to a great extent on the individual situation. Hopefully, however, the techniques, data sources, testing procedures, involvement of the neighbors, and available resources all can be generally applied.

BACKGROUND

Some background information is appropriate. The extended aeration secondary wastewater treatment system generates, at this point, a net average 1850 kg/day (4080 lbs/day) of waste activated sludge solids. As a direct result of our NPDES permit limitations, these solids may not be discharged to the Kansas River and must be disposed of otherwise. The primary disposal method is application to nearby farmland.

The raw waste contains significant amounts of sodium salts. Typically, the waste contains 12,000 mg/l sodium sulfate and 300 mg/l sodium chloride. This results in 95 kg/day (200 lbs/day) of sodium to be disposed of in the waste sludge and represents 5% of total sludge solids. The concern over the sodium content

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stems from the known detrimental effects of sodium on soils, particularly clay-bearing soils. Generally, sodium in sufficient quantity can render clays impervious to moisture. In addition, sodium can be directly toxic to plants. These conditions are not compatible with good plant growth and crop yields. The problem, then, was to determine the tolerable annual application rate of sludge and estimate the life of the application area which receives annual dosages.

DESCRIPTION OF WASTE SLUDGE

In setting up any kind of a waste disposal system, the waste material must be characterized. The sludge is generated from an imperforate basket centrifuge which removes most of the water and salt from a portion of the secondary clarifier underflow in the biological waste treatment system. The clarifier underflow contains about 1.5% solids and after centrifugation the sludge is about 7% solids. The sludge is very thixotropic and is semi-solid if the solids reach 9%.

Although thixotropic, the sludge is quite pumpable even with centrifugal pumps, provided adequate suction head is available. Positive displacement pumps are superior, however. A typical analysis of the sludge is shown in Table 1. The organic content is high as evidenced by the 75% volatile solids. The raw waste is characterized by a high cellulose content. Even though the sludge age is about 40 days in the extended aeration plant, the volatile solids remain high because of the relative indigestibility of the cellulose. The nitrogen, phosphorus, and potassium are of interest because of their value as plant nutrients. The total nitrogen is high for a waste activated sludge. The sodium, calcium, and magnesium are critical from the standpoint of soil deterioration and plant micro-nutrition. Sodium is by far the most deleterious metal in the list for three reasons: (a) the large quantity, (b) the high potential for clay bearing soil deterioration, and (c) the toxic effects on plants.

TABLE 1. Typical analysis of sludge (100% solids basis).

Volatile solids (600°C)	75.0%
Organic Nitrogen	7.1
NH_3 Nitrogen	0.1
Total Phosphorus as P_2O_5	0.4
Aluminum	0.6
Calcium	0.3
Iron	1.8
Magnesium	0.2
Manganese	1.2
Potassium	0.6
Sodium	5.2

ALLOWABLE SODIUM AND NITROGEN APPLICATION RATES

The sludge is applied to the land at a rate of about 90 tonne/ha (40 ton/a). This amount contains approximately 350 kg/ha (310 lb/a) sodium. The question arises: Is this too much sodium, and if not, how long can this quantity be applied before degradation of crop yields and/or soil occurs? When confronted with a situation like this where does one start looking for answers? There are many sources available; many of them are free or at least not too expensive: (a) Soil Conservation Service, (b) Local universities, especially land grant universities, (c) Environmental Protection Agency, (d) State and U.S. Geological Survey, (e) U.S. Department of Agriculture, (f) Technical conferences, (g) Literature, (h) Consulting firms.

We found that getting information locally is far more beneficial than looking for experts 500 miles away. Having a familiarity with local soil, weather, and geological conditions is very useful and saves time and money. It is not unusual for a "far away" consultant to come in and pursue local institutions for his information. Several references are summarized in the following pargraphs to illustrate the types of available information relevant to the sodium problem.

Whitney (1976), with the Extension Service at Kansas State University, suggested that a quantity of sodium equal to 10% of the soil cation exchange capacity (C.E.C.) can be applied every three years without damage to the soil. If it can be assumed that one-third of this quantity can be applied annually, we could apply between 280 kg/ha (250 lb/a) and 560 kg/ha (500 lb/a), depending on the soil involved. Whitney's experience is with feedlot lagoon water which is applied to the land at a rate of 61 cm/yr (24 in/yr) in conjunction with 30 cm/yr (12 in/yr) rainfall. The total amount of water applied to the land is approximately equal to the average annual rainfall for our area, but rainfall periods are sporadic and variable in quantity. When water is applied with the salt, much greater opportunity for leaching from the root zone exists. This was good background information but was not directly applicable to a sludge which contains a much higher salt concentration.

In a U.S. Department of Agriculture publication, Richards (1969) discussed the salinity hazard (as related to effects on plants) and sodium alkali hazard (as related to effects on soil). He indicated that very high salinity water is not suitable for irrigation under ordinary conditions, but may be used occasionally under very special circumstances. The soils must be permeable, drainage must be adequate, irrigation water must be applied in excess to provide considerable leaching, and very salt-tolerant crops should be selected. Very high sodium water is generally unsatisfactory for irrigation purposes except at low and perhaps medium salinity. The solution of calcium from the soil or use of gypsum or other amendments may make the use of these waters feasible. No limiting quantities of sodium were specified by Richards, but it was implied that large quantities of our sludge cannot be land applied without causing problems.

The Environmental Protection Agency (1975) makes reference to a maximum sodium adsorption ratio (SAR) of 9, above which irrigation water may adversely affect the permeability of soils. SAR is defined as follows:

$$\mathrm{SAR} = \frac{[\mathrm{Na}]}{\sqrt{\frac{([\mathrm{Ca}] + [\mathrm{Mg}])}{2}}}$$

where [Na], [Ca], and [Mg] are the concentrations of sodium, calcium, and magnesium, respectively, in milliequivalents per liter of irrigation water. Again, reference is made to limitations relative to irrigation water. This is not directly adaptable to our relatively small quantities of dewatered sludge to be applied to land. It was noted that although sodium is toxic to plants, this effect usually occurs at salt concentrations higher than will cause soil permeability problems.

Powers (1977), at Kansas State University, presented guidelines for maximum application rates of beef feedlot manure and lagoon water containing salts of sodium, potassium, calcium, and magnesium. Based on the sodium concentrations in the manure and lagoon water, the limiting sodium applications are 73 kg/ha/yr (65 lb/a/yr) and 146 kg/ha/yr (130 lb/a/yr) for manure and lagoon water, respectively. These values are somewhat lower than those of the other researchers because salts of metals other than sodium were present in significant quantities.

It became obvious that although much work had been done with saline wastes, little information was available to indicate safe application rates for our sludge.

EFFECT OF METALS ON SOILS AND PLANTS

Metals also can affect soils and plants. Metals interact with soils in different ways depending on the nature of the soil. Generally, sandy and silty soils are more porous and allow aqueous solutions of metals to pass through more readily than a clay soil. There are many different clays. However, this discussion will only span the range of characteristics at the extremes of clay crystalline structures and the resulting physical properties. These are called the 1 : 1 and 2 : 1 lattice structures.

In the 1 : 1 type, such as kaolinite, there is a silica layer and an alumina layer which share common oxygen atoms. The bond between two adjacent structures, although not as strong as internal bonds, is moderately strong. This results from hydrogen bonding between the oxygen in the silica layer and the hydroxyl group in the alumina layer. Consequently, the lattice is fixed and no expansion occurs when the clay is wetted. Cations and water do not enter between the structural units of the micelle.

At the opposite end of the scale is the 2 : 1 type lattice found in montmorillonite. In this type of clay the hydroxyl groups are buried within the structure with only oxygen atoms oriented at the outside two surfaces. Adjacent crystal units are held together by very weak oxygen cations. Montmorillonite crystals can be fractured easily and the clay can, under certain circumstances, become finely dispersed to colloidal sized particles.

Another condition that can exist in montmorillonite clays is isomorphous substitution of some aluminum atoms in the octahedral layer with magnesium atoms. This occurs at varying degrees depending on the genesis of the clay. An electronic imbalance is created when, for example, magnesium^{++} replaces alumina^{+++}. A net negative charge orients itself on the surfaces of the micelle creating an electronegative atmosphere between these surfaces. This space then has a strong attraction for cations which migrate inward to balance the charges. Some cations, depending on their size, valance, and electronegativity, have more or less tendency to move into the interlattice space. Because of this varying attraction, some cations will force others out of the lattice as they move in. This cation exchange can take place any time the cation population around a clay particle changes. The overall quantity of cations a clay can contain within the lattice is the cation exchange capacity.

According to Brady (1974), the hierarchy of strength of adsorption when the cations are present in equivalent quantities is: NH_4^+, Al^{+++}, and $Ca^{++} >$ $Mg^{++} > Na^+$ and K^+. H^+ can be found almost anywhere in the grouping depending on the amount of water present. In humid regions H^+ would occur in the first group due to probable complexing with the calcium, while the H^+ would be found in the last group in arid areas.

If one cation is present in very large quantities, as with sodium in this sludge, adsorption of this cation will dominate and displace other cations that might be present. The high percentage of exchangeable sodium in the clay micelle causes dispersion of the clay particles. Apparently, the loosely held Na^+ ions do not effectively reduce the electronegativity of the micelle, thus permitting the mutual repulsion or dispersion of the negatively charged particles. Severe dispersion results in a soil almost impervious to water. This condition is unacceptable for farmland.

Besides the indirect effect of sodium on plants through its deterioration of the soil, it can effect the plant growth directly. Sodium salts in solution contacting a plant cell causes shrinkage of the cytoplasm. This plasmolysis takes place due to the osmotic movement of cellular water to the more concentrated salt solution outside the cell. The degree of cell destruction will determine the extent of plant growth retardation.

Sodium can also disturb plant growth by replacing some of the calcium, potassium, and magnesium the plant would normally take up. Thus, the plant would suffer a deficiency of the metals. In addition, many metals which exist in the soil-plant complex qualify as micronutrients. Plants need small quantities of iron, manganese, zinc, boron, copper, molybdenum, and cobalt. In excess, these elements can cause plant growth problems. Also, various antagonistic effects can occur due to adverse combinations of metals (Brady 1974). For example, excess copper may retard the utilization of molybdenum in plants.

Other metals also can be taken up by plants. These heavy metals do not necessarily disturb the plant growth but can enter the animal or human food chain at toxic levels. The uptake rate for these metals depends on many factors such as soil pH, available soil moisture, quantity of metals applied to the soil, combination of metals applied, and plant species. Our waste activated sludge land application program is designed to determine metal uptake in the crops. This information is not discussed in this paper.

EXPERIMENTAL DESIGN TO DETERMINE SODIUM EFFECTS ON SOIL

As mentioned earlier, the sodium alkali degradation of soil is likely to occur at a lower sodium application rate than would cause salinity problems in plants. Thus, in our program, it was decided to place primary effort on determining sodium effects on the soil structure. Soils in our area are primarily clay to silty clay loam. Limited areas of sandy clay loam to loamy sand exist in some of the older river terraces. As suggested by Dickey (1976), the parameter chosen to monitor sodium effects in the soil should be the sodium adsorption ratio (SAR) using exchangeable cation concentrations expressed as milliequivalents per 100 grams of air dry soil.

To predict possible future effects and life of the sludge application area, the experimental design consisted of application rates of sludge, a chemical fertilizer control, and a control where nothing was applied. The nutrient application rates of these conditions are given in Table 2. The 1S sludge rate was equal to the rate applied routinely for the daily removal of solids from the waste treatment system. The chemical fertilizer application was normally used by the farmers in this area for wheat. The 4S sludge rate is 4 times the 1S rate and was chosen to be high enough to allow some predictions of future effects, but not so high that serious soil degradation or crop toxicity would occur before meaningful data could be obtained.

To obtain the maximum statistical significance from the data, the four test applications were arranged in a checkerboard pattern where no two adjacent squares were the same. This is illustrated in Table 3. If this pattern is rotated counter-clockwise 45° it can be seen that identical applications line up in horizontal rows. This allowed the use of typical farm equipment and the ability to plant in rows while maintaining a statistically efficient sampling pattern.

In the actual test plots, this pattern was repeated in four quarters of a larger square to establish 64 subplots. The subplots were 5.2 m (17 ft) on a side which allowed a 3.7 m (12 ft) wide diagonal path through the grid for farm equipment passage. Larger subplots were not used because they can create more statistical variation due to non-homogeneity of soil areas. In addition, the samples taken from the center of the subplot becomes less representative as the size increases.

Test plots were established in the two extremes of our soil characteristics, i.e., sandy silt loam and heavy clay. Most of the soil where sludge is routinely deposited falls between these two extremes. Two plots were laid out with identical application and sampling patterns in the two soils.

The sludge was subsurface applied with a unit attached to the back of a tank truck. The sludge was deposited 13 cm (5 in) to 20 cm (8 in) below the soil surface and became so well mixed with the soil that frequently it is difficult to find immediately after deposition. There have been no odor problems associated with this method although complete soil cover is not attained 100% of the time. Occasionally, in certain soil conditions at the end of the tank load, the subsurface unit raises higher in the soil because the weight of the load is diminished. In wet, fine-textured, heavy soil the dirt will not fall back over the sludge to provide adequate cover.

TABLE 2. Test plot application summary.

	Designation	Nitrogen		Phosphorus	
		kg/ha	(lb/a)	kg/ha	(lb/a)
1S	Low sludge	470	420	27	24
4S	High sludge	1880	1680	107	96
NC	Chemical fertilizer control	70	60	34	30
OC	Blank control	0	0	0	0

Another problem experienced with the application system was the nonlinearity of sludge application rate with truck speed. Even though the power take-off speed for the pump was linear with truck speed, the pumping rate was not. This is felt to be related to the use of a centrifugal pump for application from the truck instead of a positive displacement pump for the somewhat viscous and highly thixotropic sludge.

One of the more critical aspects of the testing operation was the precise location of sampling points. Because the application lanes were only 3.7 m (12 ft) wide, we attempted to stay within the center 50% of this lane to avoid overlap effects on the edges. A 1.9 m (6.2 ft) diameter crop sample area constrained the subplot center to be located to within ± 0.3 m (1 ft). The most effective method evaluated used permanently mounted steel marker stakes at both ends of the application lanes. Stakes similarly located with surveying equipment were posi-

TABLE 3. Arrangement of test application plots.

1S	4S	NC	OC
OC	1S	4S	NC
NC	OC	1S	4S
4S	NC	OC	1S

tioned on the sides of the plots such that a grid was formed when cotton twine was strung between appropriate pairs of stakes. Due to the diagonal sampling arrangement, every other string intersection was a sampling point.

Four samples were taken per year at each location, i.e., three soil and one crop. The wheat was sampled in late June to early July from a 2.9 m^2 (30 ft^2) circular area centered on the sample point. The sample area was circumscribed by a rubber hose for easy sample definition and cleared of weeds before harvesting the grain by hand. The samples were then threshed, winnowed, and cleared of weed seeds prior to storage for analysis. Crop yield was determined and certain metals were analyzed in the grain.

Following crop sampling, but prior to any cultivation which would disturb the samples, three soil samples were taken from each subplot: the surface 15 cm (6 in), between 30 cm (12 in), and 46 cm (18 in) from the surface, and between 61 cm (24 in) and 76 cm (30 in) from the surface. Although each subplot has a slightly different soil type, one plot (C Plot) as a whole can be described as sandy silt loam. Similarly, the other plot (D Plot) is clay.

A number of different soil sample techniques were evaluated. Varying moisture conditions and soil textures created problems with the split-spoon sampler used initially. In very dry clay the sampler would not penetrate nor be extracted readily from the soil. This led to drilling to the proper depth with an auger before using the split-spoon sampler. The last and most efficient procedure made use of a sheet metal sleeve around the auger. This prevented contamination of the sample by the sidewalls of the hole being bored. Samples were withdrawn from the top of the tube as the auger and sleeve penetrated the soil. Handles on top of the sleeve were used to extract it from the hole. All samples were deposited in zip-lock plastic bags for storage.

SOIL ANALYSES

To arrive at the sodium adsorption ratio in the soil, the exchangeable sodium, calcium, and magnesium must be determined. The total extractable cations, which includes exchangeable cations within the clay lattice and the soluble cations oriented on the surface of the crystals, were determined first. The soluble cations, found by separate analysis, were subtracted from the total extractable cations to arrive at the exchangeable cations.

The soil was first air dried and pulverized before the two extractions were run. The total extractable cations were obtained using ammonium acetate extraction and the soluble cations were determined by the saturation extract method using demineralized water. Sodium, calcium, and magnesium were determined on each extract by atomic absorption. The data were then converted to a useable form in milliequivalents per 100 grams of soil, from which the SAR was calculated.

Running all the analyses on one batch of samples from one test plot generated over 1200 pieces of data. All the data from both test plots for six years were handled by computer as were subsequent calculations, plotting, and tabulations.

All the crops were wheat with the exception of C plot in 1978. Milo was planted because the soil was too wet in late 1977 to plant wheat. No crop was harvested in 1980 from C plot because of severe storm damage.

SOIL PERMEABILITY AS AFFECTED BY SLUDGE APPLICATION

By 1982, the year after test plot work was terminated, waste treatment sludge had been applied to farmland around the plant for four years without any observable degradation of crop yields. The sodium contained in the sludge either had no negative effect on yields, or its effects may have been masked by the nutritional properties of the sludge.

At that time, soil samples were taken over the 325 acres to determine the effect of the sodium on the soil permeability. Thirty-six locations were sampled to give an average area of about ten acres per sample. This is far from being statistically satisfactory, but does give an indication of trends to be expected. All the fields sampled had four to five sludge applications with the exception of the loamy sand field which had two.

Each location was sampled at the surface (top six inches) and at about one foot deep (between 12 and 18 inches). Samples were prepared and run according to Method 41–4, Permeability of Soil to Water (Black 1965). The first 70 ml of permeate collected was used to determine the leachable sodium. The data are summarized in Table 4.

DISCUSSION OF RESULTS

In February 1985, there had been no observable degradation of crop yields in the *regular areas of daily sludge deposition*. One condition which could be construed to have affected crop yields was the excess nitrogen that resulted from the use of sludge. This caused abnormal growth in the wheat which, in turn, brought about limited lodging during wet, windy weather. Wheat is said to be lodged when it gets blown down and so entangled that it will not right itself when drying out. This reduces the harvest because it cannot be properly combined.

The chronological changes of the SAR in the top six inches of the *test plots* and the corresponding crop yields are shown in Figures 1 and 2. Figure 1 describes C plot, sand silt loam, and Figure 2 describes D plot, clay. The first sludge applications were made in late 1976. Soil and crop samples were first taken approximately 9 months after the respective fertilizer and sludge applications. The exposure of the wheat plants to the sludge was maximized because wheat planting took place just shortly after applications were made.

For the sandy silt loam test plot the following observations can be made (Figure 1):

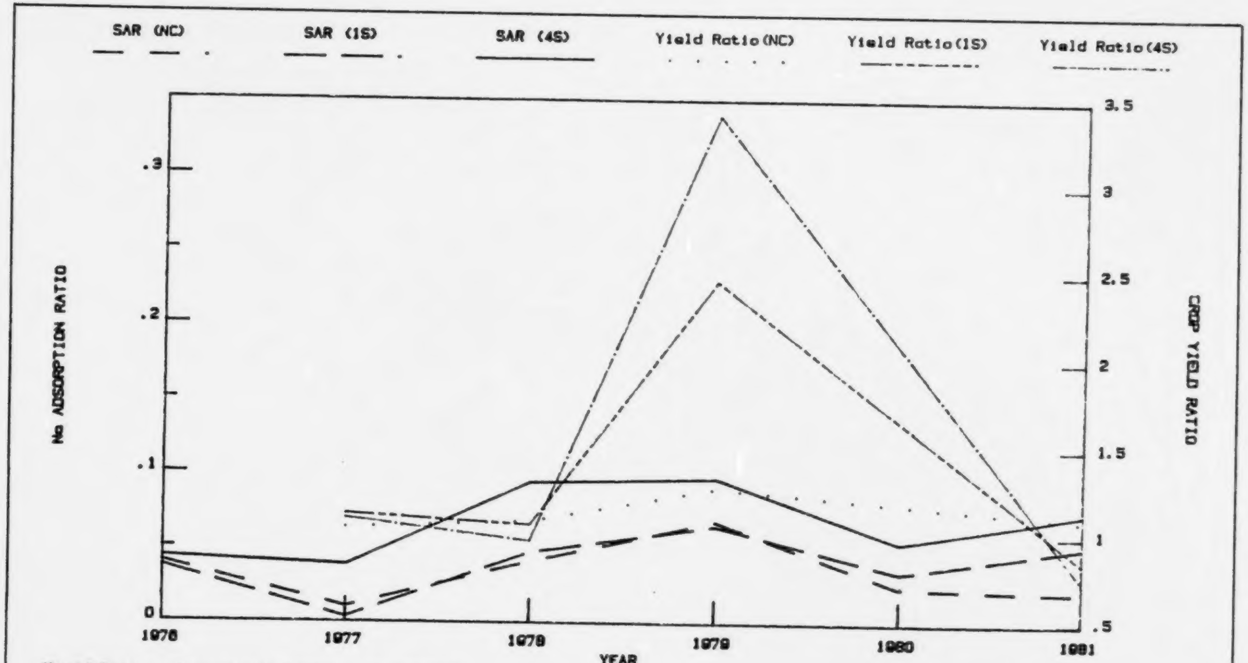
1. The SAR in the top 6 inches of soil remained relatively low for the five year period, with no apparent trend down.

2. The SAR of the single sludge application (1S) test plot was essentially identical to that of the commercial fertilizer control (NC) test plot except for the last year, when it was slightly higher.
3. The quadruple sludge application (4S) caused the SAR to roughly double the 1S SAR for the five year period.
4. The SAR for all applications showed a gentle undulating pattern, probably ascribable to rainfall and general weather patterns for the period.
5. The crop yield ratio for the 1S and 4S applications showed a significant increase over the control in 1979 and dropped slightly below the control in 1981. There was no crop in 1980. This could have helped establish a more credible trend. There is an indication of slight yield degradation after five years in the sludge amended areas, with the 4S being worse than the 1S.

TABLE 4. Soil permeability and sodium concentration by soil type.

Soil Type	Sample	Permeability to Water			Permeate Sodium	
	Depth	Sludge ml/hr	Control ml/hr	Change due to sludge %	Sludge mg/1	Sodium mg/1
Clay loam	Surface	48	75	-36	61	5
	1 Foot	25	76	-67	181	100
Silty clay loam	Surface	28	116	-76	181	9
	1 Foot	28	66	-58	209	8
Silt loam	Surface	98	210	-53	93	8
	1 Foot	120	79	+34	89	103
Sandy loam	Surface	176	236	-26	6	6
	1 Foot	312	296	+5	162	4
Loamy sand(1)	Surface	564	386	+46	60	3
	1 Foot	503	397	+27	159	2

(1) Note: This field had only 2 sludge applications while the rest had 4 to 5.



Yield Ratio = Crop yield (bu/ac) for specific application / crop yield (bu/ac) for no-application control.

FIGURE 1. SAR and crop yield; sandy silt loam (C Plot), top 6 inches.

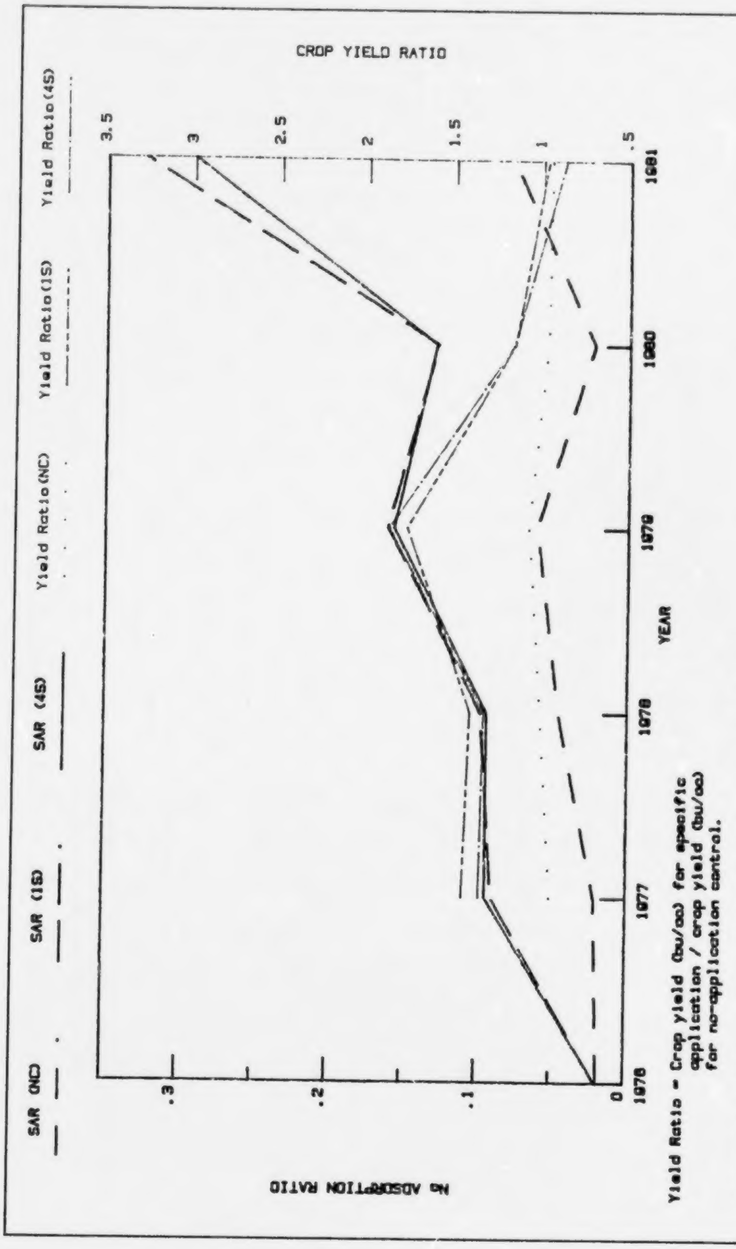


FIGURE 2. SAR and crop yield; clay (D Plot), top 6 inches.

For the clay soil test plot the following observations can be made (Figure 2):

1. The SAR for the commercial fertilizer (NC) control test plot was very similar to the SAR of the NC control in the sandy silt loam test plot. This is to be expected.
2. The SAR values for the 1S and 4S applications test plots were similar to each other but significantly higher than that of the NC control test plot.
3. The 1S SAR showed a distinct upward trend over the five years.
4. The SAR of the 4S application test plot also showed an upward trend with time.
5. The maximum SAR was 0.33, about three times the maximum in the sandy silt loam plot.
6. The 1S and 4S crop yields for the first three years exceeded the control by 40 to 60%. They dropped gradually during the last two years to nearly equal the control.

The change in SAR as affected by depth into the soil in the sandy silt loam test plot is depicted in Figures 3a, 3b, and 3c, for the fertilizer control, single sludge application, and the quadruple sludge application, respectively. The project involved two controls: no applications and commercial fertilizer. The no application (OC) control is shown on all three plots for comparison. Figures 3a, 3b, and 3c should be reviwed as a set. The following observations can be made:

1. The SAR of the fertilizer control (NC), Figure 3a, was almost identical to the OC control of the five years.
2. With one sludge application, Figure 3b, the SAR increased somewhat with time, but showed little difference with soil depth until the fifth year when the sodium appeared to be migrating to the two-foot depth.
3. With the quadruple sludge application (4S), Figure 3c, the rate of rise of the SAR is distinctly higher than that for the 1S application. There is a more apparent accumulation of sodium at the one-foot level for the first three years. It then gradually migrates at a higher rate to the two-foot depth after two more years.

The SAR as affected by the soil depth in the clay test plot is shown in Figures 4a, 4b, and 4c, for the fertilizer control, single sludge application, and the quadruple sludge application, respectively. The following observa tions can be made:

1. There was no significant difference between the SAR of the fertilizer control and the no-application control over the five years.
2. The single and quadruple sludge applications caused almost identical SAR patterns in the soil profile (Figures 4b and 4c). Both applications showed a slight upward trend in SAR. There was no significant difference in the exchangeable cations and the SAR, between the 1S and 4S applications.
3. A pattern that showed up after four years for both the 1S and 4S applications was that the SAR was higher nearer the surface of the soil profile. The SAR at the surface was nearly double that at the two-foot depth. It appeared that the

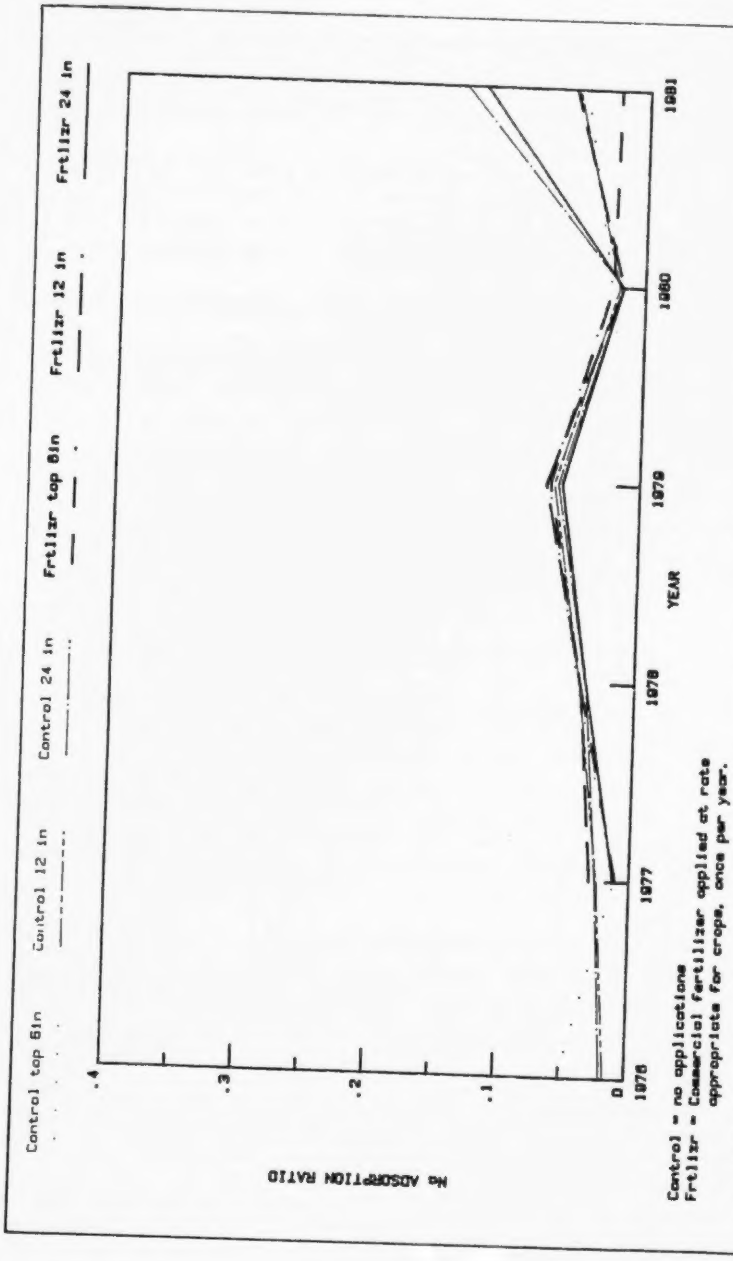


FIGURE 3A. SAR as affected by soil depth; sandy silt loam (C Plot), fertilizer control.

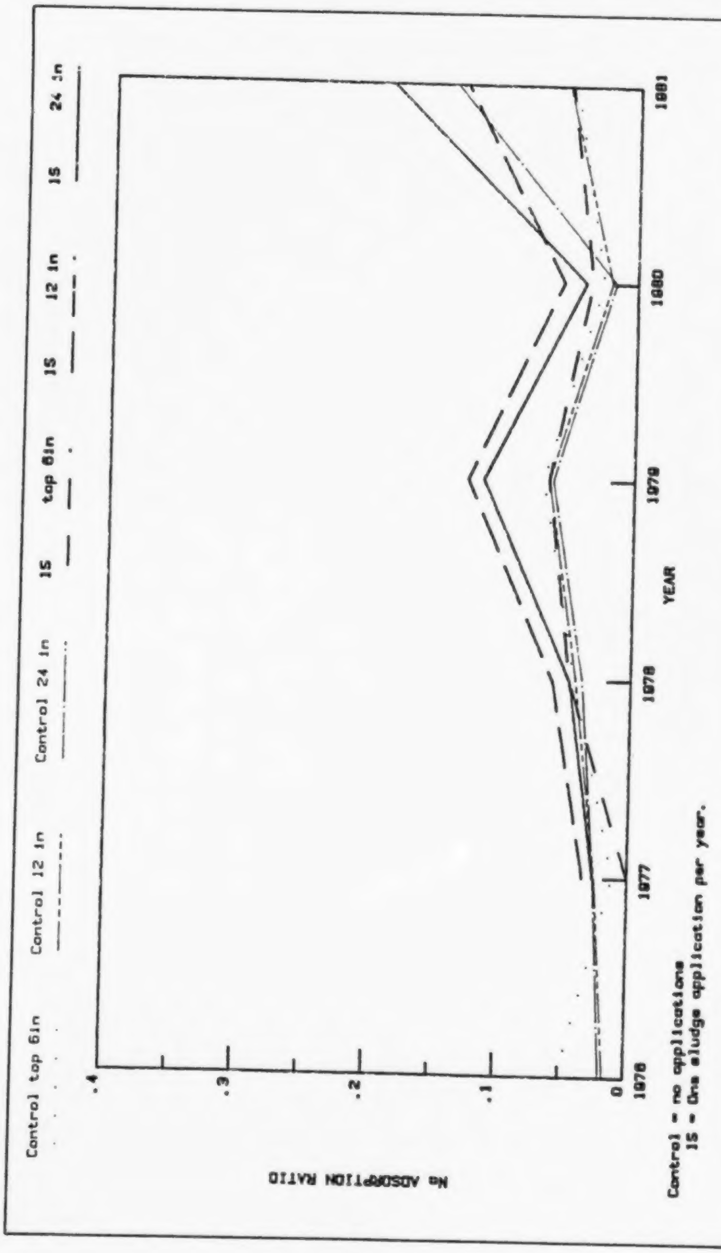


FIGURE 3B. SAR as affected by soil depth; sandy silt loam (C Plot), one sludge application.

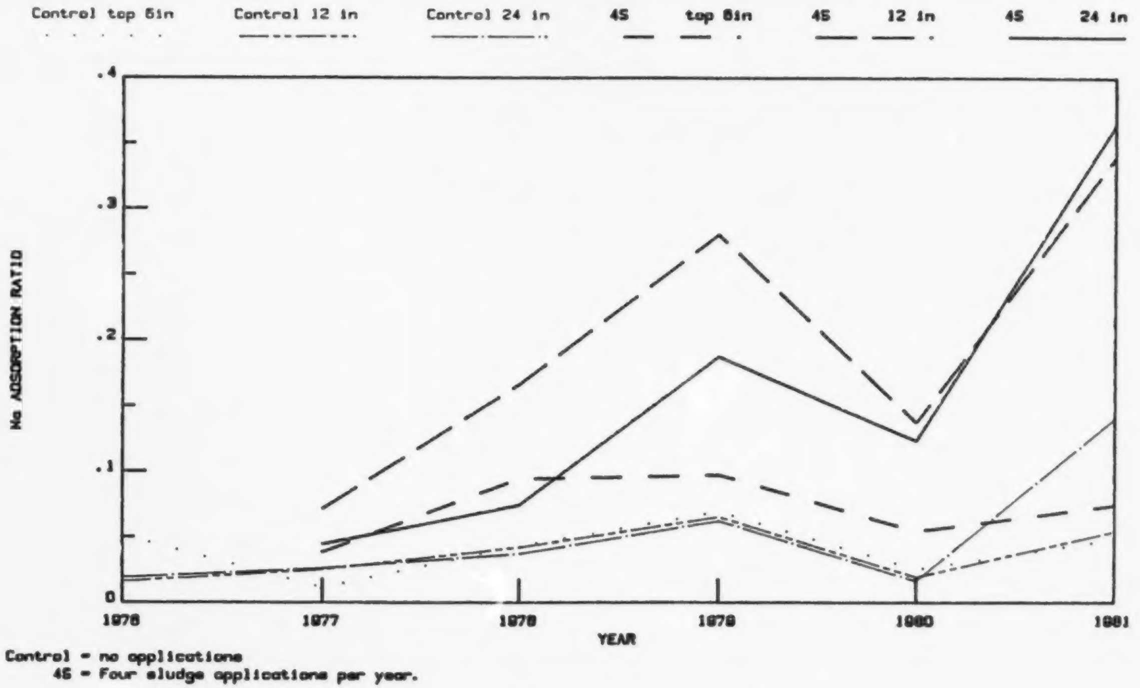


FIGURE 3C. SAR as affected by soil depth; sandy silt loam (C Plot), four sludge applications.

sodium became bound in the clay structure to the extent that less sodium remained sufficiently soluble to migrate to lower soil horizons.

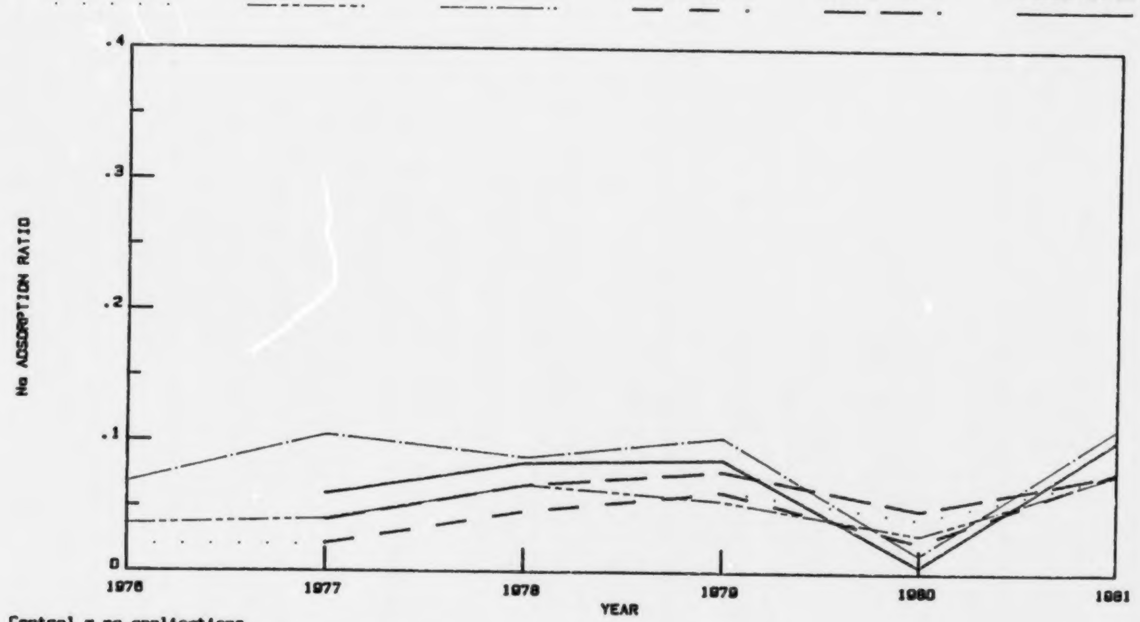
The effects of the sludge application (over 325 acres of land) on the soil permeability to water are shown in Table 4. In addition, the leachable sodium present at two soil horizons is presented. A pattern became apparent when the soil was categorized according to the clay content of the soils, or more precisely, the practice size of the soil. The following observations can be made:

1. As one scans the data from fine soil (clay loam) down to coarse soil (loamy sand), the change in permeability due to sludge amendment goes from negative to positive. The sodium in the sludge affects the clay bearing soils more than the coarse grained soils.
2. The permeate sodium indicated that the soluble sodium in the soil profile did *not* correlate well with the change in permeability. This supported the original hypotheses of this paper which proposed a relationship between the soil physical properties and the exchangeable cations bound within the soil micro-structure.
3. In all cases except the silt loam, the soluble sodium was concentrated below the surface horizon. The one foot deep samples had soluble sodium concentrations that were all higher than the concentrations in the surface. The one exception was the silt loam which showed essentially the same soluble sodium concentration at both levels.
4. The two controls had abnormally high soluble sodium levels. This may have been caused by surface runoff or subterranean migration.
5. The permeability to water generally increased for sludge amended and control samples as the soil particle size increased, i.e., as the soil progressed from clay to sand.

CONCLUSIONS

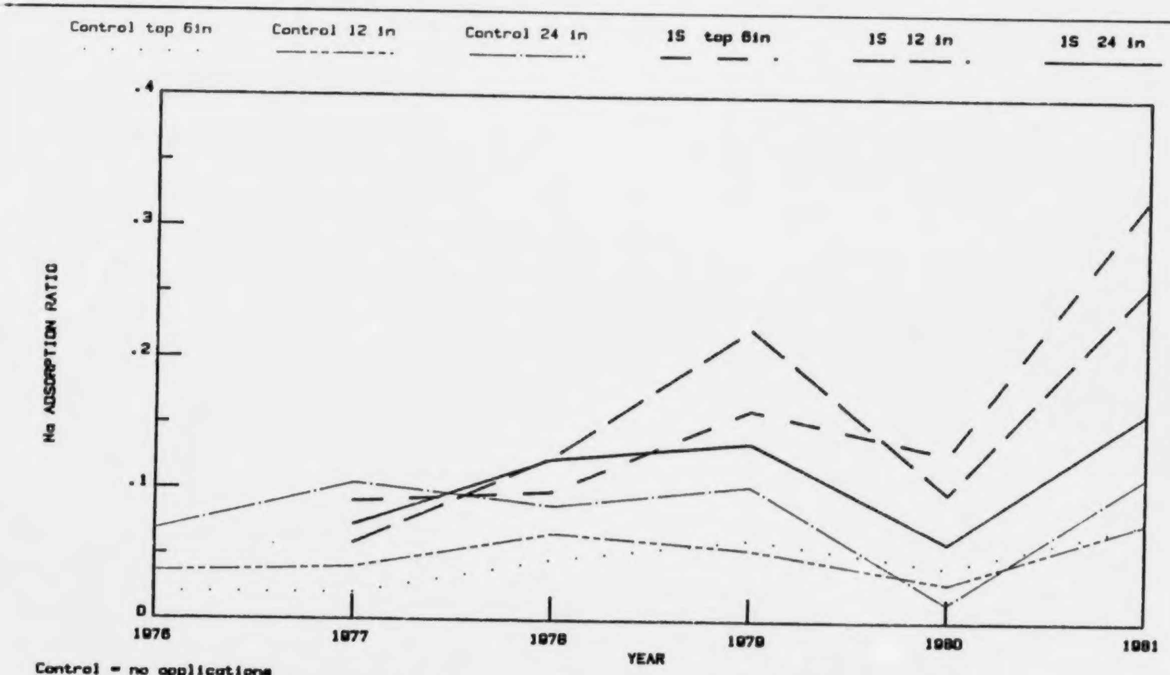
General

1. The SAR based on exchangeable cations in the soil provides a parameter that may be used to evaluate soil properties.
2. Using good management, the sludge from this plant may be applied to farmland without permanent reduction of crop production capacity.
3. For all sludge application rates and soil types, the sludge amended crop yields exceeded the yields from the commercial fertilizer control plots except for the sand silt loam in the fifth year when it dropped slightly.
4. Permeability to water was affected negatively by the sludge in the clay soils while that of the sandy soils showed an improvement.
5. The soil permeability did not correlate with soluble sodium, indicating that the exchangeable cations in the soil micro-structure are responsible for permeability differences.
6. Soluble sodium tended to concentrate below the surface for all soil types.



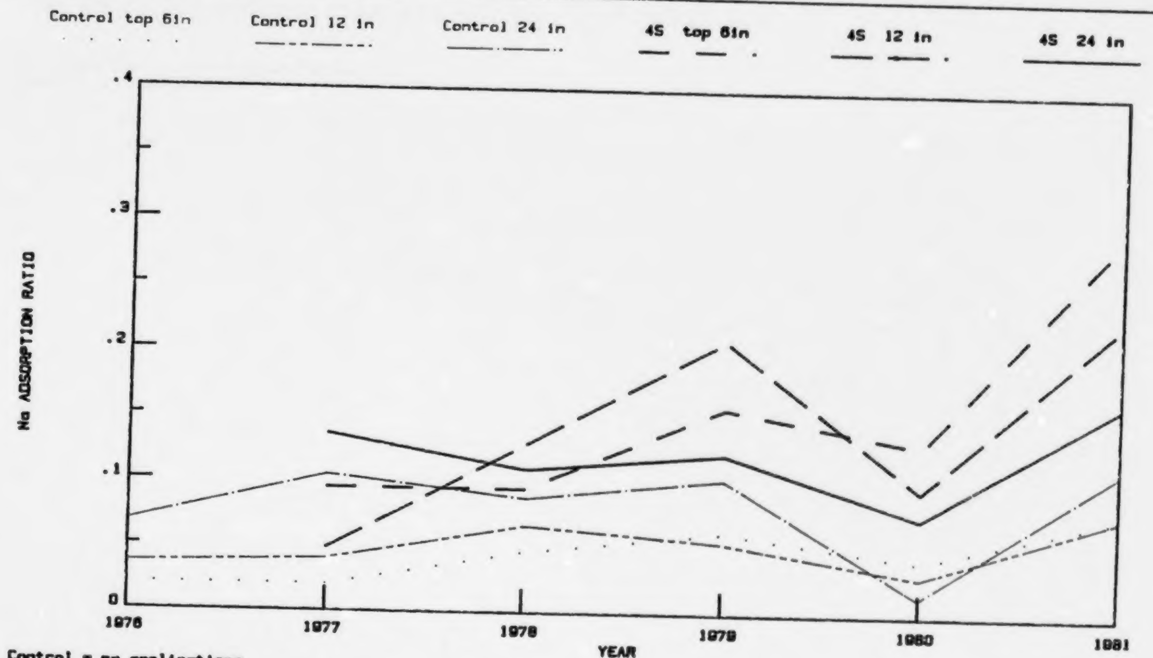
Control = no applications
Frtlizr = Commercial fertilizer applied at rate
appropriate for crops, once per year.

FIGURE 4A. SAR as affected by soil depth; clay (D Plot), fertilizer control.



Control = no applications
1S = One sludge application per year

FIGURE 4B. SAR as affected by soil depth; clay (D Plot), one sludge application.



Control = no applications
4S = Four sludge applications per year.

FIGURE 4C. SAR as affected by soil depth; clay (D Plot), four sludge applications.

For sandy silt loam

1. There was no correlation of crop yield with SAR in the soil over five years of annual sludge applications.
2. The rate of SAR increase with time was greater with the higher sludge application rate.
3. There was little difference in SAR at the one- and two-foot levels, but both were significantly higher than the surface SAR.

For clay soil

1. The SAR showed a steady increase with time over the entire five year period.
2. After three years of annual sludge applications the clay soil crop yields dropped as the SAR increased. The crop yields in the sludge soils, however, never dropped significantly below the yields from commercial fertilizer control plots.
3. The rate of SAR increase with time was no greater for the quadruple sludge applications than for the single applications.
4. The SAR was highest at the surface and generally decreased at deeper soil horizons.

CORRECTIVE MEASURES

This study has determined enough about the effects of sodium in the sludge being applied to the farmland at an early enough point in the program to preclude any permanent damage to the soil. In order to sustain good soil with its current crop-producing capacity, our plans call for the following measures:

1. Spread sludge thinner over more land.
2. In older sludge amended areas, concentrate new depositions on the sandier soils.
3. Apply calcium to all clay-bearing soils. This can be in the form of gypsum or lime, depending on the pH requirements of the soil.
4. Break soil to a depth of two feet to allow more rapid percolation away from the root zone. Deep plowing may be in order in certain areas depending on the type of underlying soil horizons.

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LAND TREATMENT PRACTICES IN THE PETROLEUM INDUSTRY

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This paper presents a review of land treatment practices in the petroleum industry. The study was conducted by Environmental Research & Technology, Inc. (ERT) for the American Petroleum Institute (API) and included the participation of several major oil companies. Design, operating, and performance data was collected for: 14 full-scale refinery land treatment facilities, and 4 pilot-scale refinery land treatment facilities.

The data are summarized in this paper to present the range of design and operating criteria for land treatment facilities in the petroleum refining industry and describe the performance of these systems.

BACKGROUND

Land treatment has been used as a waste treatment and disposal technology by U.S. petroleum refineries for greater than twenty-five years. In addition, the technology has been used in recent years by the exploration and production sector of the petroleum industry and has been applied on a limited scale to waste oils and for the clean up of oil spills resulting from crude oil transportation.

Figure 1 shows the location of many of the petroleum industry land treatment facilities in the U.S. The Environmental Protection Agency (EPA) has estimated that approximately 100 land treatment facilities exist in the U.S. petroleum industry, primarily in the refinery sector. About one-third of all U.S. refineries have full-scale or pilot-scale land treatment facilities and more refineries are expected to follow suit. In addition, 26 to 38 Canadian refineries and at least 10

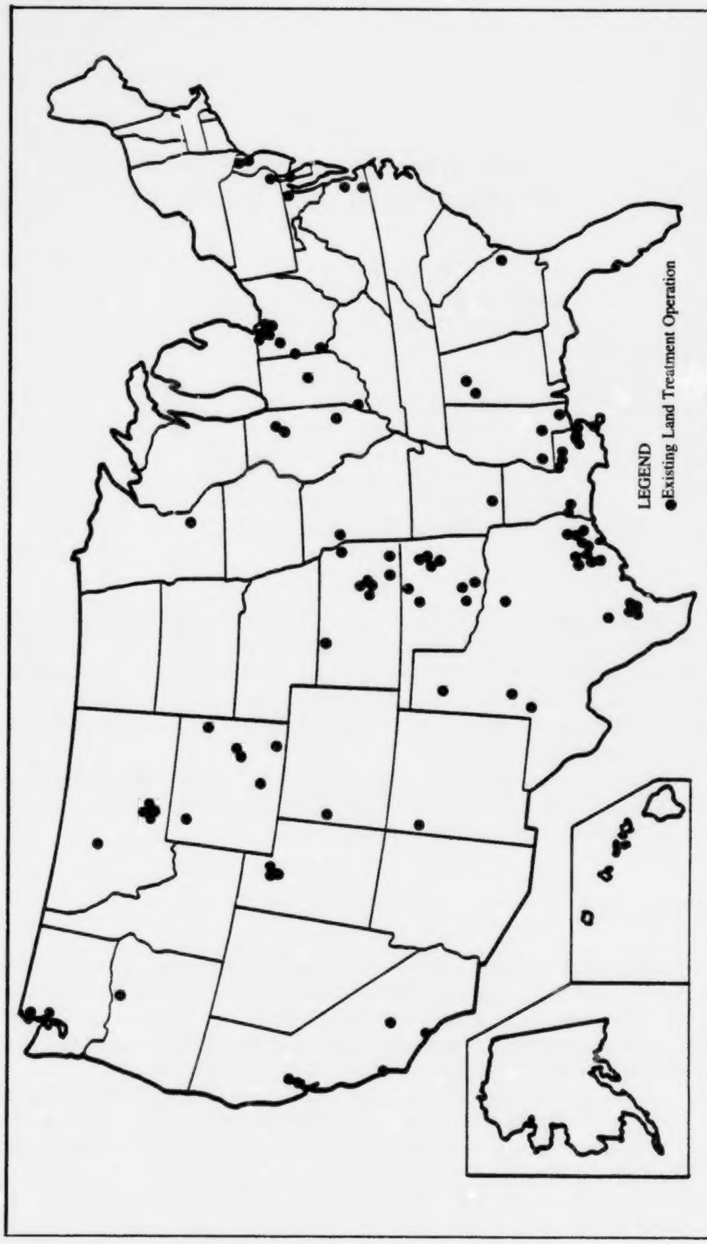

LEGEND
● Existing Land Treatment Operation

FIGURE 1. Location of petroleum industry hazardous waste land treatment facilities in the United States (Brown 1981).

refineries in Europe use land treatment as an environmentally sound, cost effective, waste disposal technology (Beak Consultants Ltd. 1981).

Land treatment uses the assimilative capacity of the soil to decompose and contain the applied waste in the surface soil layer (usually the top 15 to 30 centimeters or 6 to 12 inches). The upper soil layer is the zone of incorporation. The incorporation zone, in conjunction with the underlying soils where additional treatment and immobilization of the applied waste constituents occur, is referred to as the treatment zone. The treatment zone in the soil may be as much as 1.5 meters (5 feet). Soil conditions below this depth generally are not conducive to oxidation of the applied waste constituents. The transformations, biological oxidations, and immobilization will occur primarily in the zone of incorporation. Acceptable conditions for biological degradation and immobilization in the soil are important. Figure 2 identifies some of the major transformations that occur at a land treatment site.

DESIGN AND OPERATING CONSIDERATIONS

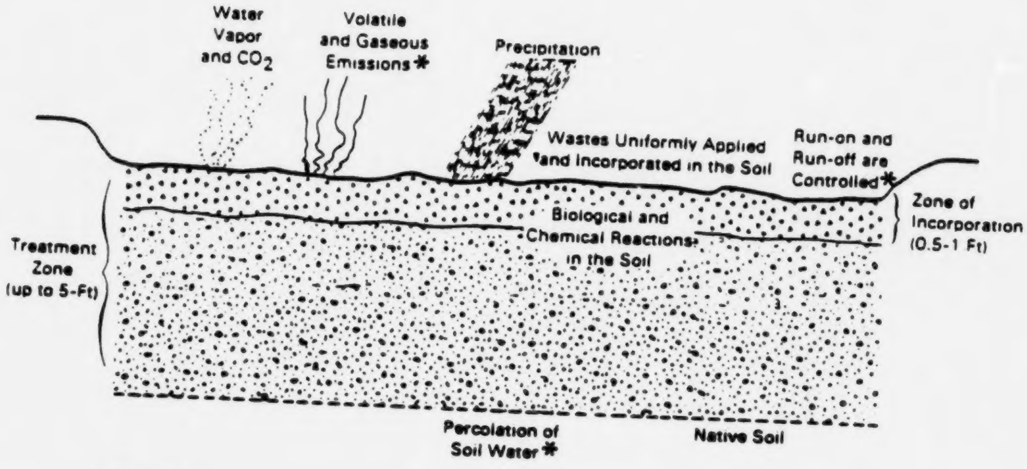
The successful performance of land treatment depends upon an understanding of the site and waste characteristics that affect the degradation, transformation, and immobilization of the wastes applied at the land treatment site. The waste and site characteristics that are pertinent to the design and management of land treatment site as well as the principal operational factors are noted in Table 1.

Waste Characteristics

The land treatment process is suitable for the treatment and disposal of most oily waste material generated by a refinery as well as wastewater treatment biosludge (Knowlton and Rucker 1979). Table 2 lists the refinery wastes which are land treated by the full-scale and pilot-scale facilities reviewed in this study. The list is intended to be representative rather than comprehensive and should not be considered as exclusive. The wide range of waste types which have been successfully land treated illustrates the broad applicability of the process.

Refinery wastes vary considerably in physical composition. Most refinery wastes can be handled as a pumpable fluid or slurry, although some refineries have installed dewatering equipment and generate a sludge cake.

The oil phase is often characterized on the basis of hydrocarbon fractions. Table 3 presents a hydrocarbon analysis of the oil phase for wastes which are commonly land treated. The oil phase is primarily composed of saturate and aromatic hydrocarbon fractions which are rapidly removed in land treatment systems. Heavy metals commonly found in significant concentration (greater than 10 ppm) in land treated refinery wastes include (Engineering-Science, Inc. 1976): chromium, copper, lead, nickel, zinc.


Water
Vapor
and CO_2
Volatile
and Gaseous
Emissions *
Precipitation
Wastes Uniformly Applied
and Incorporated in the Soil
Run-on and
Run-off are
Controlled *
Zone of
Incorporation
(0.5-1 Ft)
Treatment
Zone
(up to 5-Ft)
Biological and
Chemical Reactions
in the Soil
Percolation of
Soil Water *
Native Soil

*Land treatment minimizes the uncontrolled migration of pollutants to the environment

FIGURE 2. Illustrative inputs and transformations at a land treatment site.

Site Characteristics

Land treatment of refinery wastes has been successfully practiced in all the major climatic regions of the United States, Europe, and Canada under a wide range of hydrogeologic conditions. Table 4 identifies important site characteristics of the full-scale refinery facilities reviewed. The data suggest that there are

TABLE 1. Land treatment design and operating considerations for petroleum industry wastes.

A. Pertinent Waste Factors

Physical Composition
Organics
Metals

Salts
Nutrients
pH

B. Pertinent Site Factors

Soil Characteristics
- Topography
- Soil texture
- Soil moisture content
- Cation exchange capacity
- Soil pH
- Soil microorganisms
- Nutrients

Climate
- Temperature
- Precipitation

Hydrogeology
- Depth to seasonally high water table
- Depth to usable aquifer
- Proximity to surface water

C. Operational Factors

Waste Application
- Oil loading
- Hydraulic loading
- Frequency of application
- Method of application

Storm Water Management
- Run-on/run-off control

Waste Incorporation
- Depth of incorporation
- Frequency of cultivation

Soil Amendments
- Nutrients
- Moisture
- pH control

Monitoring
- Operational
- Environmental

very few site limitations which cannot be overcome with the appropriate design and operation of land treatment facilities. Rules specifying ideal site characteristics are not very realistic. It is more important to consider how critical site characteristics are addressed in the design and management of the facility.

Climate is a particularly significant site feature which affects the design and operation of a land treatment facility. Climate has an impact on: (a) appropriate application rates, (b) the frequency of waste applications, (c) storage requirements, (d) runoff system design, and (e) system performance. Little or no oil

TABLE 2. Types of wastes applied to the full scale refinery land treatment facilities reviewed.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Oil-water separator sludge	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Dissolved air flotation sludge	X	X				X			X				X	
Induced air flotation sludge		X							X			X		
Tank bottoms	X	X	X	X	X	X	X	X	X	X		X		X
Slop oil emulsion solids			X	X			X	X	X	X				X
Oily sludge		X	X		X	X			X				X	X
Filter clays		X	X		X		X		X	X		X		X
Biological sludges	X		X			X	X		X				X	
Cooling tower sludge							X		X			X		
Lime sludge				X					X					
Coker blowdown sludge														X

Source: American Petroleum Institute, 1983.

degradation takes place when the soil temperature is near freezing. With proper design and operation, however, land treatment can be successful in colder climates as well as in humid and warm climates.

Laboratory studies have indicated that optimal soil temperatures for biodegradation of oil wastes are 20°C or greater (Bartha and Dibble 1979). Biological activity decreases as the temperature decreases. Little oil oxidation occurs when the soil temperature is near freezing.

Soil temperature for bare surface soils are commonly greater than ambient temperatures by 2–5°C during daylight hours. Surface soil temperatures at land treatment sites may exceed ambient temperatures by 5-8°C due to increased microbial respiration and the increased radiant energy due to the darker soils which result from oil application (Lewis 1980).

For the purposes of this study, the term degradation month has been developed. A degradation month is defined as a month during which the average air temperature exceeds 10°C. This concept permits useful comparisons to be made between land treatment facilities with significantly different climatic conditions. The concept was developed for comparison purposes only and does not imply

TABLE 3. Physical compositon of refinery wastes.

	Typical Compositon, Percent		
Waste Type	Oil or Hydrocarbon	Water	Solids
Oil-water separator sludge	8	73	19
Tank bottoms*	60	37	3
Air flotation froth	7	88	5
Biological treatment sludges	3	92	5
Cooling tower sludge	1	74	25
Spent treating clay	17	9	74
Waste lime sludge	0	73	27

*Data are for crude, distillate and residual tanks.

Source: Engineering Science, 1976.

TABLE 4. Summary of site charcteristics at refinery land treatment facilities.

Site Parameter	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H	Site I	Site J	Site K	Site L	Site M	Site N
Location	Mont.	Calif.	N.J.	Ill.	Miss.	La.	Wash.	Wash.	Texas	Texas	Texas	Texas	Okla.	Okla.
Land Area (acres)	11	6	8	30	12	7	14.5	10	50	N.D.	N.D.	1.5	17	19
Degradation* (months/year)	6	12	7	7	12	12	7	6	12	12	12	12	9	8
Net Water Budget** (inches/year)	-10.0	-15.7	19.7	11.0	15.1	16.6	-0.5	13.2	4.3	-18.0	-36	-29.5	2.4	4.4
Surface Soil Texture	silty clay	fine sand	N.D.	silty clay	fine sand	sandy silt	fine sandy clay	silty clay loam	clay	fine sandy loam	clay	clay	silty loam	claey silt

* Degradation month is defined for comparison purposes as a month when the average air temperature is greater than 50°F.
** Net Water Budget = precipitation - evaportranspiration.

Source: American Petroleum Institute 1983.

TABLE 4. Continued.

Site Parameter	Site A	Site B	Site C	Site D	Site E	Site F	Site G	Site H	Site I	Site J	Site K	Site L	Site M	Site N
Location	Mont.	Calif.	N.J.	Ill.	Miss.	La.	Wash.	Wash.	Texas	Texas	Texas	Texas	Okla.	Okla.
Cation Exchange	11.3	5.5	N.D.	10-25	8	24	15	5.5	35	8.7	11.4	57	10-20	11
pH	6.6-8.1	6.6-7.0	7.0-7.8	7.7-8.2	6-8	7	6.9	5.7	7.4-8.3	7.5-8.0	6.4-7.3	8.0	6.5-7.2	7
Depth to Seasonally High Water Table (ft)	5	42	2	2	5	3-5	3	N.D.	12	N.D.	N.D.	N.D.	N.D.	19.5
Depth to Usable Aquifer (ft)	N.D.	130	N.D.	22	350	219	45	N.D.	50	N.D.	N.D.	200+	12	N.D.
Previous Land Use	agriculture	former lagoon	former sanitary landfill	agriculture	N.D.	N.D.	N.D.	N.D.	agriculture	N.D.	former tank farm	N.D.	N.D.	N.D.

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* Degradation month is defined for comparison purposes as a month when the average air temperature is greater than 50°F.
** Net Water Budget = precipitation - evaportranspiration.

Source: American Petroleum Institute 1983.

that oil degradation will not occur during months when the average air temperature is less than 10°C.

Site preparation activities at most facilities include: (a) removal of site vegetation, (b) the separation of the site into several plots, and (c) the construction of an elevated roadway/dike around the facility to control surface runoff and permit site access. Many land treatment facilities are graded to promote surface drainage and collect site runoff.

The types of site modifications instituted at existing land treatment facilities vary depending on the existing site characteristics. Examples of these modifications are presented in Table 5.

Operations

Land treatment facilities vary considerably in terms of: waste application rate, method of waste application, soil amendments used, storm water management.

Operation plans for land treatment facilities have been developed to consider unique site characteristics as well as economic factors. Waste application methods vary from subsurface injection of fluid sludges to surface application of liquid and semisolid sludges. Wastes are not applied when the ground is frozen or excessively wet.

The depth of cultivation defines the zone of incorporation for facilities which apply wastes only to the surface. The common cultivation equipment used is disk

TABLE 5. Site modification that may be used at land treatment sites.

Site Modification	Reason
Tree and rock removal	Site access, ease of tilling
Topsoil addition	Improve soil infiltration capacity
Subsurface drainage tiles	Prolonged high water table
Perimeter drainage ditches	Intercept seasonally high perched water table
Soil pH adjustment	Low pH
Contouring, terracing, grading	Steep slopes
Road construction, berm and dike construction, external perimeter drainage ditches	Intercept and divert off-site run-on, contain on-site run-off, provide access

harrows and rototillers. Rototillers are preferred by some facilities as they are thought to accomplish more thorough mixing of the waste and soil. Rototillers, however, are also considered more difficult and expensive to maintain. Several passes over the field may be needed to provide a homogeneous soil waste mixture.

The frequency of cultivation for most facilities is once per waste application event. Facilities which operate with high oil loading rates may culivate two or three times per waste application event to enhance soil aeration and waste/soil contact. Less frequent cultivation is reported for land treatment sites which receive biosludges with little or no oil content.

Many terms are used in the literature to identify the quantity of oil applied to a land treatment site. The standard convention is to report surface application rates as barrels of oil per acre and volumetric application rates (considering the zone of incorporation) as percent oil in the soil or pounds of oil per ft^3 of soil. These English units will be used throughout this paper to permit convenient comparisons to other reported data. The appropriate metric conversions are:

barrels/acre x 0.393 = $meters^3$/hectare
$pounds/foot^3$ x 0.062 = $kilograms/meter^3$

Figure 3 illustrates the relationship between incorporation depth, surface application rates, and volumetric application rates. It can be seen that an application rate of 400 barrels of oil per acre approximately equals 5.8 pounds of oil per ft^3 of soil or 7.2% oil in the soil at an incorporation depth of 6 inches.

Table 6 summarizes oil application rates and the frequency of application reported for refinery land treatment facilities. In order to compare the data between facilities, the effects of temperature have been considered by identifying the degradation months for each site. The annual oil loading was then divided by the number of degradation months to identify the oil loading per acre per degradation month.

The use of soil amendments varies considerably among land treatment facilities and is site and waste specific. Agricultural lime or waste lime sludges are applied at facilities where surface soil has a low pH. Nutrient applications (in particular nitrogen) may enhance oil degradation rates in the initial period of operation. However, many facilities, perticularly those with low oil application rates, do not consider nutrients necessary to optimize the performance of the facility. Supplemental irrigation has been used on a limited basis at some facilities located in semiarid areas which use high oil application rates. Moderate amounts of fertilizers have been applied at a few facilities.

All land treatment facilities are required to contain and manage site runoff. The collected runoff may be allowed to evaporate on site, or it may be discharged to the wastewater treatment system.

Monitoring is a particularly important aspect of land treatment operations. Most facilities routinely monitor the soil for pH, soil moisture content, oil and grease content, and nutrients in order to schedule waste application events and determine the need for supplemental soil amendments. In addition, if the facility is applying a listed hazardous waste, the operators are required to monitor the

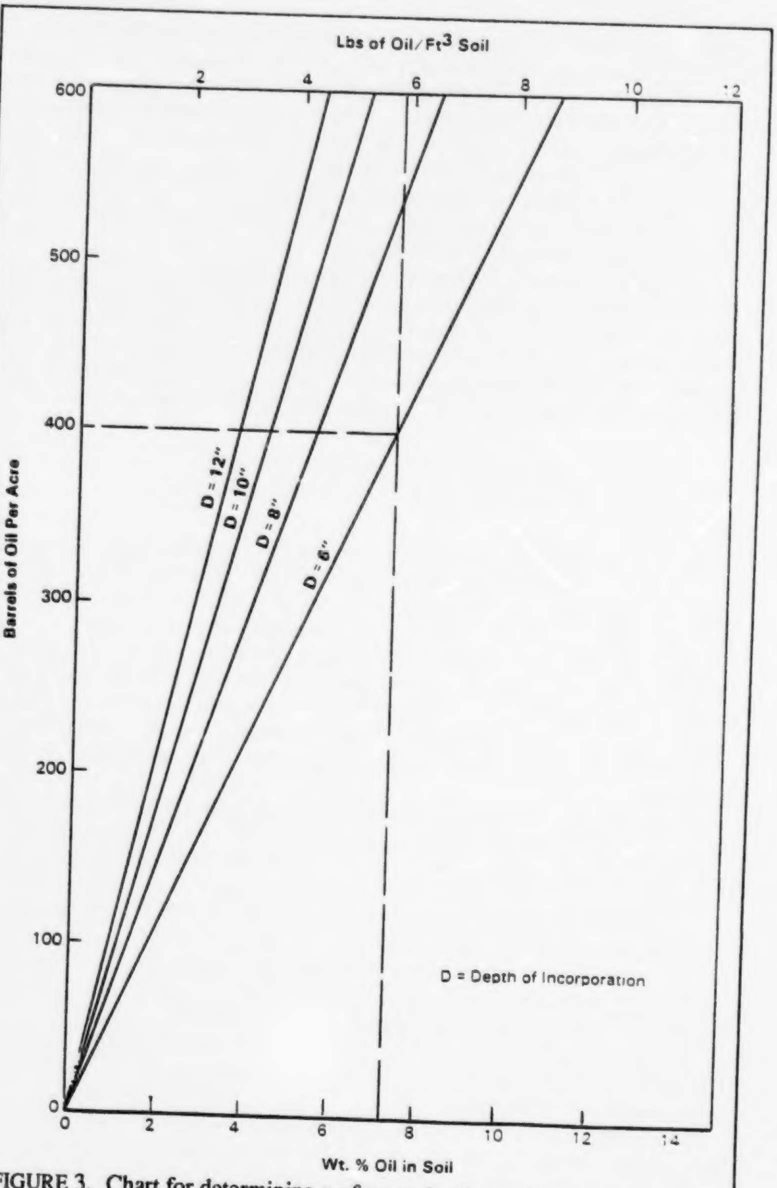

FIGURE 3. Chart for determining surface and volumetric loading rates for various depths of incorporation.

TABLE 6. Oil application rates and frequency of application at full scale refinery facilities.

		A Depth of Incorporation	B Annual Oil Loading		C Number of Applications	D[a] Oil Loading Per Application		E Number of Degradation	F[b] Oil Application/ Degradation Month	
Site	Location	(inches)	Barrels/acre	lbs/ft^3 [c]	Per Year	Barrels/Acre	lbs/ft^3 [c]	Months/Year	Barrels/Acre	lbs/ft^3 [c]
A	Montana	6	70	0.98	2-3	23-35	0.33-0.49	6	12	0.16
B	California	12	1900	13.35	52	36	0.26	12	158	1.11
C	New Jersey	6-8	650	7.82	2-4	160-325	1.95-3.9	7	93	1.12
D	Illinois	6	100	1.40	N.D.	N.D.	N.D.	7	14	0.20
E	Mississippi	8	840	8.85	24	35	0.37	12	70	0.74
F	Louisiana	8	380	4.00	5-6	65-75	0.67-0.80	12	32	0.33
G	Washington	6-8	650	7.82	52	12	0.15	7	93	1.11
H	Washington	12	280	1.97	N.D.	N.D.	N.D.	6	47	0.33
I	Texas	6-8	220	2.65	10-12	18-22	0.22-0.26	12	18	0.22
J	Texas	8	680	7.16	10-12	56-68	0.60-0.72	12	57	0.60
K	Texas	6	400	5.62	N.D.	N.D.	N.D.	12	33	0.47
M	Oklahoma	6-8	500	6.00	10-12	42-50	0.5-0.6	9	56	0.67
N	Oklahoma	6	110	1.54	6	18	0.26	8	14	0.19

[a] D = B - C

[b] F = B - E

[c] pounds of oil per cubic foot of incorporation zone

N.D. - no data available

soil and soil pore water in and beneath the treatment zone and groundwater to evaluate the performance of the facility.

PERFORMANCE

Land treatment systems are operated so as to degrade and immobilize hazardous waste constituents within the treatment zone. The performance of a facility can be quantified on the basis of: oil reductions observed over time and, accumulation and immobilization of waste constituents.

Oil Reductions

Tables 7 and 8 present estimated oil reduction rates for full-scale and pilot-scale facilities. The estimates are more reliable for pilot-scale facilities because documenting oil reduction rates was a specific objective of these studies. The full-scale data, however, provide important background information concerning oil reductions under real world operating conditions.

The estimated annual percent oil reduction observed at the full scale facilities ranges from 58–94% and typically ranges from 70–90%. Figure 4 indicates that the percent oil reductions observed are not affected by the oil application rate within the range of application rates considered. The full-scale data compares favorably with pilot scale data which ranges from 63–94% oil reduction with the exception of pilot scale Facility 4, which was operated on a single batch loading basis (Meyers and Huddleston 1980). The oil reduction at Facility 4 is shown in Figure 4 as point 4. The low oil reduction rate achieved by Facility 4 illustrates the effect of frequency of oil and application on oil reduction rates.

At pilot scale Facility 2 (Table 8) the plot receiving a composite of oily and biological sludge had the lowest oil reduction rate of the test plots evaluated at this facility (Weldon 1982). Facility 2 is illustrated in Figure 4 as point 2. The operators of this experiment suggested that the lower rates were a result of preferential utilization of the biosludge as a substrate by the microorganisms. Continued monitoring of the soil, after the pilot study had been completed, indicated that 82% of the applied oil had been reduced after one year.

Figure 5 compares the oil applied and the oil removed per degradation month. The figure indicates that the amount of oil degraded increases as the application rate increases up to an application rate of at least 1.4 lbs. of oil applied per ft^3 of soil per degradation month. This would correspond to approximately 70 to 150 barrels of oil applied per acre per degradation month depending on the depth of incorporation and operating procedure.

The estimated oil reduction reported in Tables 7 and 8 and illustrated in Figure 4 and 5 represent the average annual percent oil reduction over the operational lifetime of the facility. This data is skewed by the first year of operation for most facilities. The initial start-up period is characterized by low oil reductions until the soil microbial population becomes acclimated to the hydrocarbons as a growth substrate. Once the system is acclimated, an apparent steady state bal-

TABLE 7. Oil reduction rates at full scale refinery facilities.

			Annual Oil Loading		Estimated Annual Oil Reduction			Estimated Oil Reduction/ Degradation Month[2]		
Site	Location	Years in Operation	Barrels/ Acre	lbs/ft^{3}*	Barrels/ Acre	lbs/ft^{3}*	Degradation Months/Year	Barrels/ Acre	lbs/ft^{3}*	Percent Reduction
A	Montana	9	70	0.98	41	0.57	6	6.8	0.09	58
B	California	2	1,900	13.35	1,460	10.28	12	122	0.86	77
C	New Jersey	8	650	7.82	455	5.47	7	65	0.78	70
D	Illinois	9	100	1.40	70	0.98	7	10	0.14	70
F	Louisiana	5	380	4.00	332	3.52	12	20	.29	88
H	Washington	8	280	1.97	182	1.26	6	30	0.21	64
I	Texas	2	220	2.65	163	1.96	12	14	0.16	74
J	Texas	6	680	7.16	640	6.73	12	53	0.56	94
K	Texas	3	400	5.62	350	4.94	12	29	0.41	88
M	Oklahoma	12	500	6.00	400	4.80	9	44	0.53	80
N	Oklahoma	5	110	1.54	70	0.98	8	9	0.12	64

[1] Annual oil reduction estimated on the basis of
(a-b) c, where a = total amount of oil applied over facility lifetime (estimated)
b = oil remaining in soil (measured)
c = number of years facility has been in operation.

[2] Oil reduction/degradation month estimated on the basis of the average annual oil reduction divided by the number of degradation months/year.

* Pounds of oil per cubic foot of incorporation zone.

Source: American Petroleum Institute 1983.

TABLE 8. Oil reduction rates at pilot scale refinery facilities.

Site Location		Years in Operation	Types of Waste Added	Average Annual Oil Loading		Estimated Annual Oil Reduction[1]		Degradation Months/Year	Estimated Oil Reduction/ Degradation Month[2]		Percent Reduction
				Barrels/ Acre	lbs/ft³*	Barrels/ Acre	lbs/ft³*		Barrels/ Acre	lbs/ft³*	
1.	Ohio	3	Composite Centrifuged Oily Sludge	735	7.72	595	6.25	6	99	1.04	81
			API Separator Sludge	690	7.25	607	6.38	6	101	1.06	88
2.	Oklahoma	3	Composite Oily Sludge	1,140	11.97	832	8.74	9	93	0.97	73
			Composite Oily Sludge	730	7.68	569	5.99	9	63	0.66	78

[1] Annual oil reduction estimated on the basis of
(a-b) c, where a = total amount of oil applied over the lifetime of the facility
b = oil remaining in soil
c = number of years facility has been in operation.

[2] Oil reduction/degradation month estimated on the basis of the average annual oil

* Pounds of oil per cubic foot of incorporation zone; reduction divided by the number of degradation months/year.

Source: Weldon 1900; Mayers and Huddleston 1940.

TABLE 8. Continued.

Site Location	Years in Operation	Types of Waste Added	Average Annual Oil Loading		Estimated Annual Oil Reduction[1]		Degradation Months/Year	Estimated Oil Reduction/ Degradation Month[2]		Percent Reduction
			Barrels/ Acre	lbs/ft^3*	Barrels/ Acre	lbs/ft^3*		Barrels/ Acre	lbs/ft^3*	
		Composite Oily and Biological Sludge	540	5.67	340	3.57	9	38	0.40	63
3. Texas	3	DAF Sludge	162	1.70	152	1.60	12	12	0.13	94
		Separator Sludge	177	1.86	129	1.36	12	11	0.11	73
		Tank Bottoms Sludge	345	3.62	314	3.29	12	26	0.27	91
4. Oklahoma		Composite Oily Sludge	380	3.99	163	1.71	8	20	0.21	43

[1] Annual oil reduction estimated on the basis of
(a-b) c, where a = total amount of oil applied over the lifetime of the facility
b = oil remaining in soil
c = number of years facility has been in operation.

[2] Oil reduction/degradation month estimated on the basis of the average annual oil

* Pounds of oil per cubic foot of incorporation zone; reduction divided by the number of degradation months/year.

Source: Weldon 1900; Mayers and Huddleston 1940.

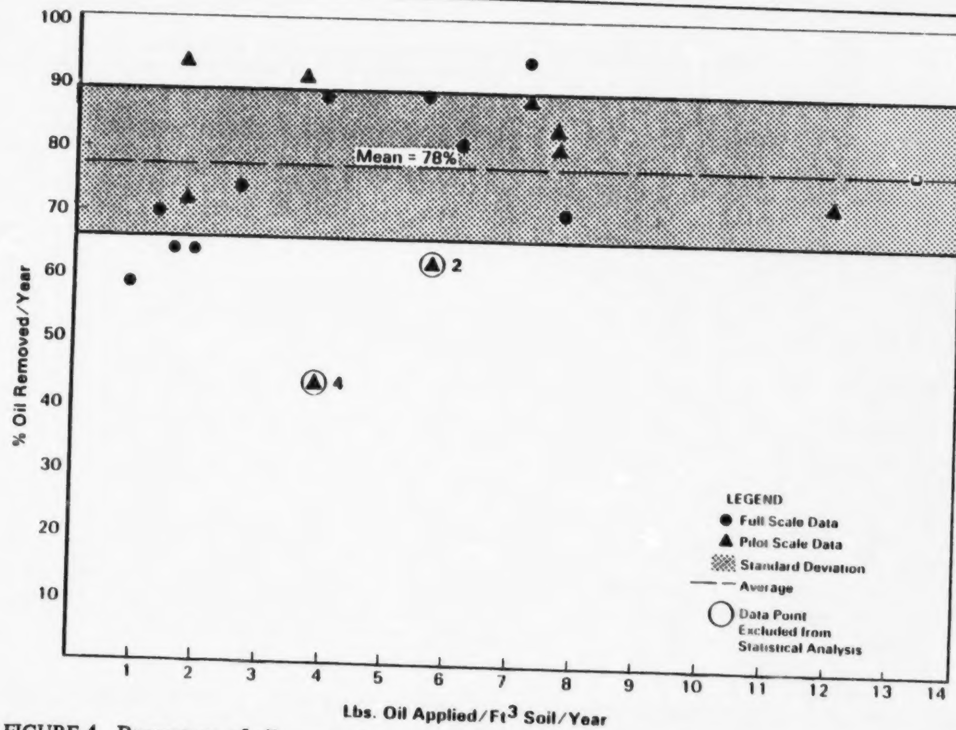

FIGURE 4. Percentage of oil removed versus oil application rate (API 1983).

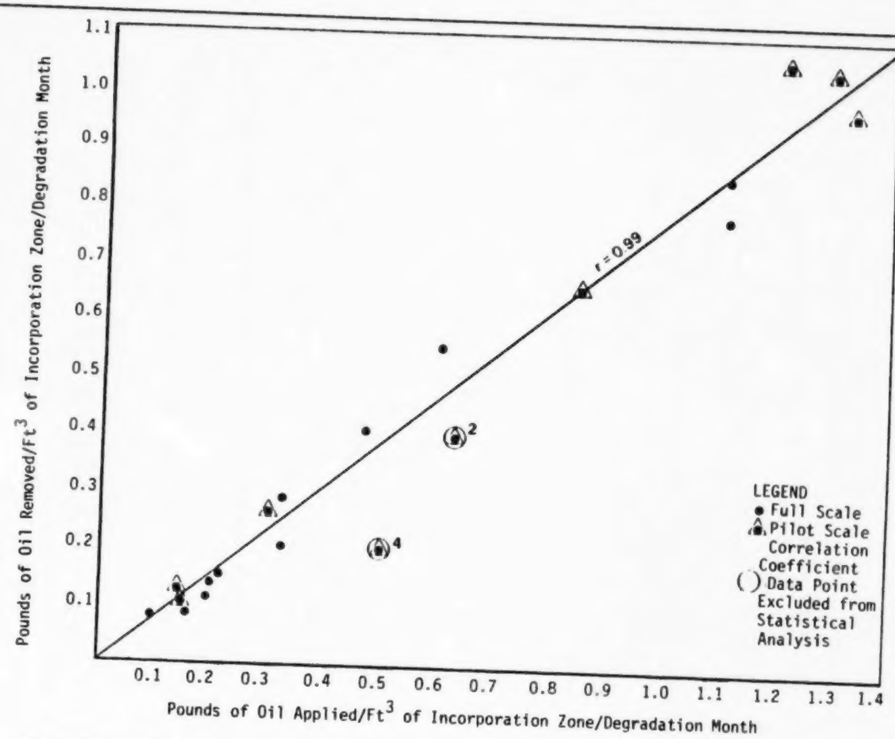

FIGURE 5. Oil removal rates as a function of oil application rates (API 1983).

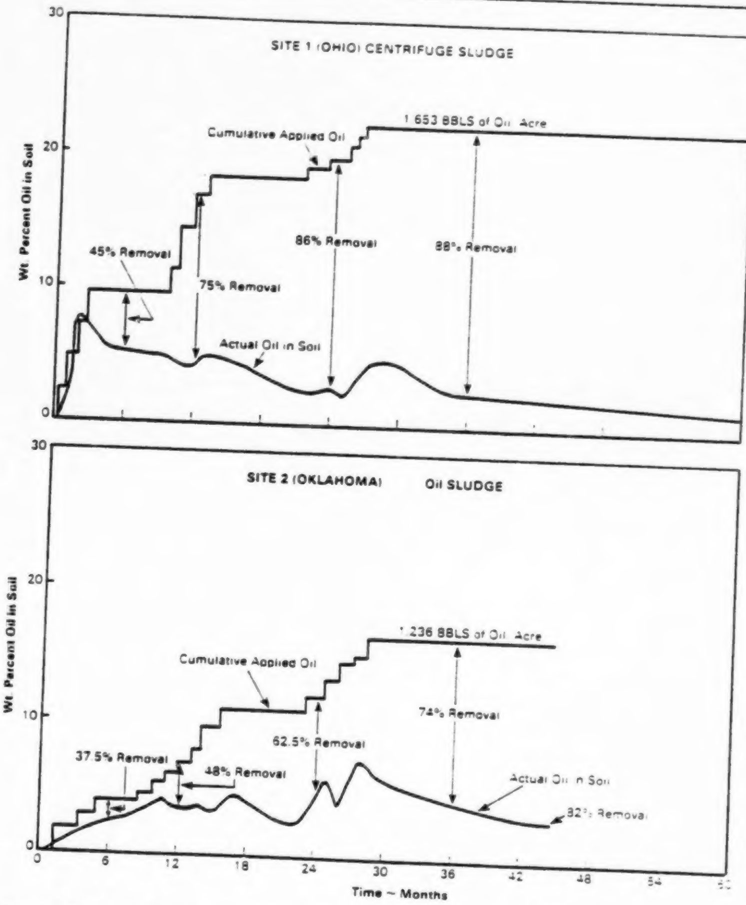

FIGURE 6. Oil removal rates at two pilot scale facilities (Weldon 1982).

ance is established where annual oil applications approximate annual oil reductions.

This point is illustrated in Figure 6 which compares the cumulative oil applied to the oil measured in the soil over a three-year period for two different pilot-scale facilities. Each facility is distinctly different in terms of climate, waste application rate, and types of waste applied. Each facility, however, experienced a low oil reduction in the initial year of operation followed by relative steady state conditions (i.e., the amount of oil in the soil at the beginning of the second year approximated the amount of oil in the soil at the end of the second and third year). The oil content in the soil at all of the facilities continued to degrade after the final application.

An average oil reduction of 70 to 90%, therefore, does not imply that 10 to 30% of the annual oil loading accumulates in the soil each year. The data suggest that a mass balance on an active system which had been in operation more than two years would indicate that 10 to 30% of the cumulative oil applied to the facility had accumulated in the soil over the lifetime of the facility. This accumulation would continue to degrade after waste applications were terminated.

Accumulation and Subsurface Migration of Hydrocarbons

Figure 7 illustrates the oil content with depth for several full-scale faciities. The profiles are typical of refinery land treatment facilities. A wide variation in oil content is evidenced among facilities in the zone of incorporation (up to 8%). However, the soil oil content below the zone of incorporation decreases rapidly with depth. The maximum extent of oil migration for the facilities reviewed was less than 1.5 feet below the zone of incorporation and well within the aerobic treatment zone of the facility (Brown and Deuel 1982).

Available data from pilot scale facilities indicates that accumulated oil will continue to degrade for several years after oil applications have terminated (i.e., the land treatment facility is closed). Figure 6 indicates that approximately a 50% reduction in soil oil concentrations was observed over a two-year period at closed pilot scale facilities which had oil concentrations in the soil greater than 3% at the time of the waste application (Weldon 1982). No effort was made to stimulate degradation after the last waste application at any of these plots (i.e., no cultivation or soil amendment took place).

Evaluation of the hydrocarbon fractions in the accumulated oil at land treatment facilities suggests that as the soil oil content decreases, the concentration of heavy aromatics and asphaltenes increase in the soil. The result is that there is an increase of these compounds in the soil compared to the saturated and light aromatic hydrocarbon fraction of the applied soil (Huddleston and Creswell 1976). A mass balance indicates, however, that the heavy aromatic and asphaltenes do degrade but at much slower rates that the overall oil reduction rate (Weldon 1982).

Accumulation and Subsurface Migration of Metals

In general, waste application at full-scale land treatment facilities has resulted in an accumulation of metals in the zone of incorporation. Tables 9 and 10 present the mean and range of metal concentrations observed at land treatment sites and background soils near land treatment sites. Background concentrations were measured on nearby soil where wastes had never been applied. The concentrations in the surface foot of land treatment site soils are significantly higher than background values for chromium, copper, lead, and zinc. All the metals are attenuated with depth, generally within one to two feet below the zone of incorporation.

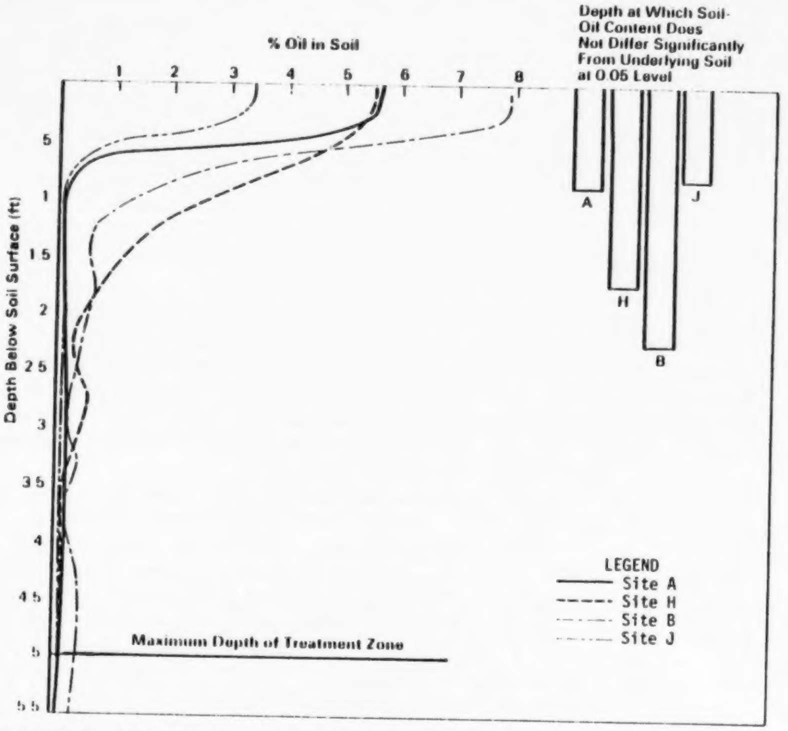

FIGURE 7. Oil content in soil with depth (Brown 1982).

Figure 8 illustrates the relationship between background concentrations and on-site concentrations of the metals evaluated in Tables 9 and 10 at the treatment zone boundary (3 to 5 feet below the soil surface). The line on the graph represents an ideal 1 to 1 relationship between average background concentrations and average on-site concentrations (if metal migration is small below the treatment zone boundary, the on-site concentration should equal the background concentration). As would be expected, there is some variability between background and on-site soils due to the variability between soil types. The graph, however, clearly illustrates that the applied metals are immobilized within the treatment zone for the facilities reviewed.

Accumulation and subsequent migration of metals has not been a concern at the land treatment facilities reviewed. Several metals have been observed to exceed background values at most land treatment facilities, however, their low solubility limits subsurface migration resulting in the immobilization of the applied metals within the treatment zone.

Accumulation and Subsurface Migration of Salts

Land treatment has resulted in the accumulation and subsurface migration of certain salts at some facilities. A slight increase in the sodium content of surface soils has been noted as well as an increase in the electrical conductivity of the surface soil (Brown and Deuel 1982). The pH of surface soils has typically been altered by one pH unit. The change is generally an increase although at two facilities the pH has been noted to decrease.

The extent of accumulation and migration of salt (as measured by electrical conductivity—EC) is strongly influenced by climate. Sites located in arid areas have the highest EC values in the surface soil (3 to 10 millimhos/cm) whereas sites located in humid areas typically had EC values less than 1 millimho/cm. None of the levels observed were high enough to impair microbial degradation.

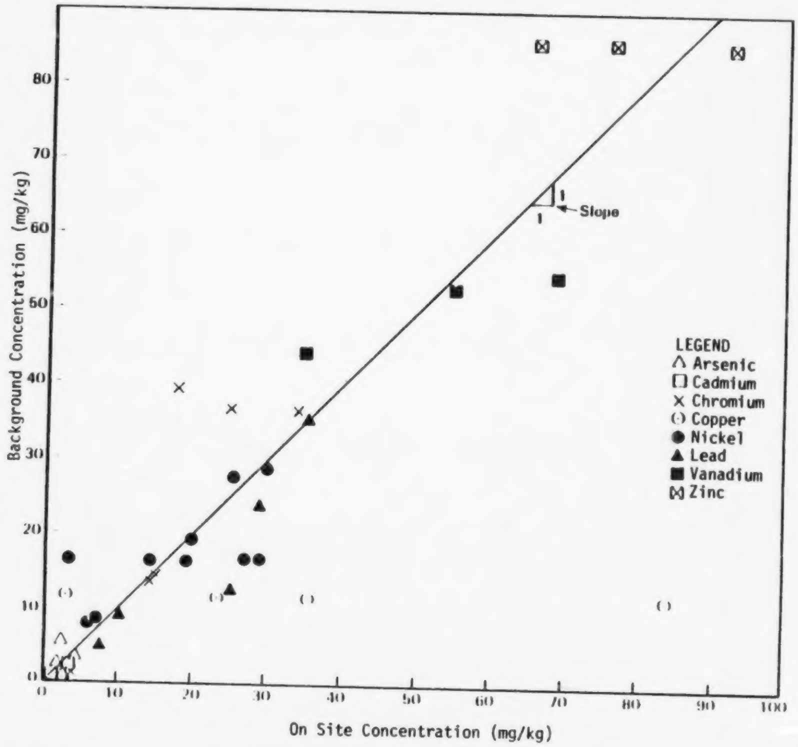

FIGURE 8. Comparison of heavy metal concentrations of background and site soils at a 3- to 5-foot depth (API 1983).

TABLE 9. Metal content of active refinery facilities. *

Depth Below Ground Surface (ft.)	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
	mg/kg Dry Soil Weight								
0-1	2.76 0.41-16.3 15 21	5.11 0.11-10 23 29	277 1.5-1468 30 48	89 2.3-260 15 27	2.11 0.04-11 23 29	17.5 2.5-50 24 29	718 2.5-5560 30 48	45.5 2.5-121 15 20	306 7.3-1041 22 34
1-3	2.14 0.06-11.3 16 36	5.00 0.03-10 19 39	71.8 1.4-315 23 49	32.1 2.4-75 7 13	0.55 0.01-1.8 21 41	18.6 2.9-50 21 41	119 1.47-1250 23 49	46 2.5-130 18 38	180 3.7-1175 16 22
3-5	1.89 0.063-6.6 9 15	2.15 0.01-4 14 22	76.3 1.5-248 17 25	33.7 4.0-84 8 10	0.42 0.01-1.2 14 22	17.0 4.0-30.9 13 20	19.5 0.84-40 17 25	57.3 2.5-94.4 13 20	72.6 15.3-138 8 10

*Data reported as:
Average
Range
No. of individual plots sampled
No. of total samples collected

Source: American Petroleum Institute, 1983.

TABLE 10. Metal content of background soils near refinery facilities.*

Depth Below Ground Surface (ft.)	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
	mg/kg Dry Soil Weight								
0-1									
	2.74	3.51	65.8	24.3	0.675	17.1	40.5	52.1	92.1
	0.08-6.2	0.07-10	1.7-244	6.3-42	0.07-1.6	1.8-50	4.91-150	2.5-109.3	16.3-156
	7	9	12	5	9	10	12	9	6
	16	20	23	7	20	18	23	17	9
1-3									
	1.79	2.42	30.1	8.1	0.81	15.9	24.5	58.6	74.2
	0.1-4.8	0.03-8	2-146	7.4-8.7	0.01-1.5	4.0-36	1.1-88.5	2.5-111	9.8-176
	7	7	9	2	8	9	9	9	4
	27	27	33	6	28	28	33	28	9
3-5									
	2.07	1.75	37.9	12	0.74	18.7	18.7	84.3	85
	0.11-3.9	0.02-4.0	2.07-152	–	0.01-1.4	7.9-29.0	1.26-40	44.1-152	–
	2.07	7	7	1	7	6	7	6	1
	13	16	16	3	16	13	16	13	3

*Data reported as:
Average
Range
No. of individual plots sampled
No. of total samples collected

Source: American Petroleum Institute, 1983.

SUMMARY

Land treatment of select petroleum refinery wastes is a cost effective, environmentally sound technology. The process is suitable to a wide variety of wastes and site conditions. The successful environmental performance of refinery land treatment facilities under a wide range of site and operating conditions is well documented.

Oil removal efficiencies at most facilities range from 70 to 90%. A linear relationship exists between oil removal rates and oil loading rates within the range of oil loadings evaluated (10 to 158 barrels of oil per acre per degradation month). The data indicates that oil reductions at full-scale facilities have ranged from 0.09 to 0.86 lbs. of oil per ft^3 per degradation month.

Certain metals, most notably lead and chromium, have accumulated above background levels in surface soils at some land treatment facilities. The metals are attenauted with depth and generally approximate background concentrations within one to three feet of the zone of incorporation; thus, they are immobilized within the treatment zone. The accumulation of total metals at land treatment sites has not resulted in significant increases in the concentrations present in the leachate extracted from these soils. The low solubility of the metals suggest that they are of limited concern at most facilities.

The salt content of some land treatment site soils has increased significantly above background. This effect is most pronounced in arid areas and tends to decrease with soil depth. Salts may be migrating at some sites; but where this effect has been noted, the water table aquifer is naturally saline, and there has been no apparent impact on the quality of the groundwater.

Land treatment of refinery waste significantly alters the chemical composition of soil. Certain slowly degraded hydrocarbons and inorganic constituents of the applied wastes may accumulate in the soil. The accumulation of these constituents is addressed in the closure and post-closure plans for these facilities.

The data indicate that land treatment has been highly effective treatment and disposal technology for select refinery wastes. The facilities reviewed have attained a high treatment performance with respect to the degradation and immobilization of applied waste constituents and have successfully met environmetal performance standards.

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THE LAND TREATABILITY OF APPENDIX VIII ORGANICS PRESENTED IN PETROLEUM INDUSTRY WASTES

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This paper summarizes the results of a study prepared for the American Petroleum Institute concerning the land treatability of Appendix VIII constituents. The paper focuses on the treatability of Appendix VIII organics in petroleum industry wastes. Results of this study, however, are applicable to other hydrocarbon wastes.

The objectives of this study were to: (1) identify Appendix VIII consitutents known or suspected to be present in petroleum industry wastes which are land treated; (2) summarize literature data concerning the degradation and immobilization of the identified constituents; and (3) prepare a methodology which could be used to evaluate those constituents which are most difficult to treat.

BACKGROUND

The petroleum industry has successfully used land treatment to treat and dispose of select wastes for over twenty-five years. Many of these petroleum industry land treatment facilities apply wastes which are classified as hazardous under 40 CFR 261 and therefore are subject to the regulations specified under the Resource Conservation and Recovery Act (RCRA). These existing and new land treatment facilities must apply for a RCRA permit to continue operations. As part of the permit application each individual facility must develop a treatment demonstration engineering report.

Figure 1 identifies the significant tasks and information which is necessary to prepare and complete a Part B permit application. The treatment demonstration engineering report must provide treatability data for the hazardous constituents and identify the principal hazardous constituents (PHCs) which need to be evaluated in an unsaturated zone monitoring program. Only those wastes which can be degraded, transformed, or immobilized such that the hazardous constituents are not expected to emerge from the treatment zone may be applied to the facility. The treatment demonstration must therefore: (1) identify the hazardous constituents which are present in the waste in significant concentrations, and (2) provide

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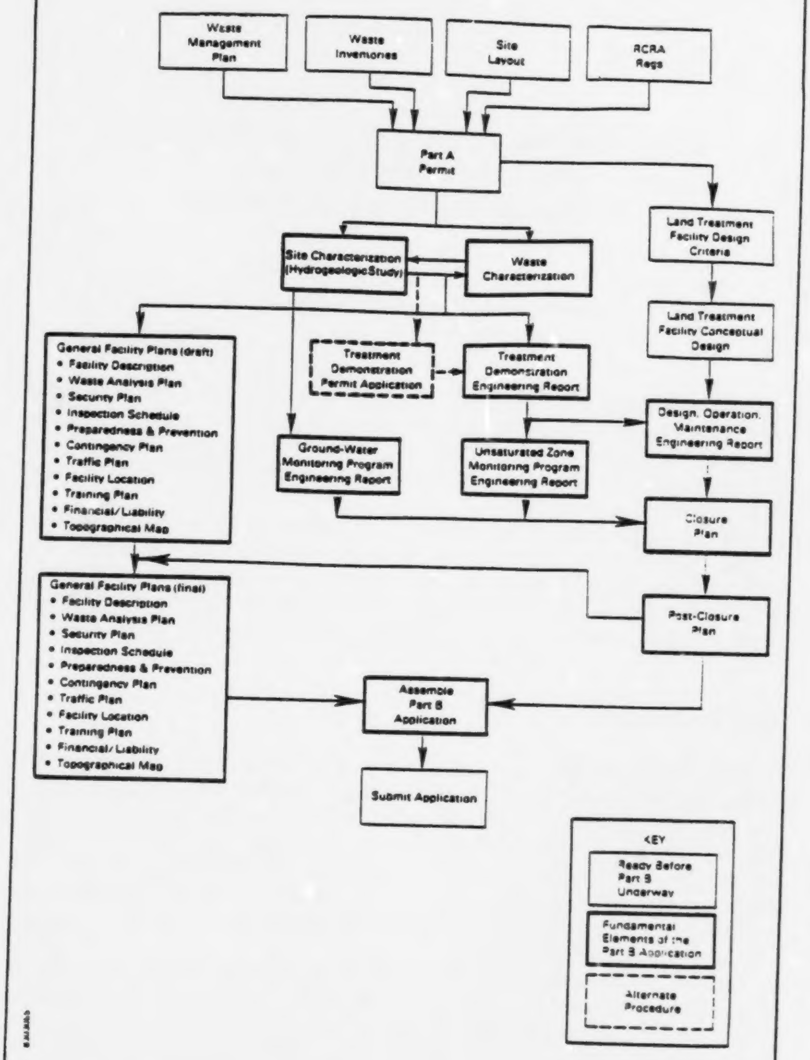
Waste Management Plan
Waste Inventories
Site Layout
RCRA Regs
Part A Permit
Land Treatment Facility Design Criteria
Site Characterization (Hydrogeologic Study)
Waste Characterization
Land Treatment Facility Conceptual Design
General Facility Plans (draft)
• Facility Description
• Waste Analysis Plan
• Security Plan
• Inspection Schedule
• Preparedness & Prevention
• Contingency Plan
• Traffic Plan
• Facility Location
• Training Plan
• Financial/Liability
• Topographical Map
Treatment Demonstration Permit Application
Treatment Demonstration Engineering Report
Design, Operation, Maintenance Engineering Report
Ground-Water Monitoring Program Engineering Report
Unsaturated Zone Monitoring Program Engineering Report
Closure Plan
General Facility Plans (final)
• Facility Description
• Waste Analysis Plan
• Security Plan
• Inspection Schedule
• Preparedness & Prevention
• Contingency Plan
• Traffic Plan
• Facility Location
• Training Plan
• Financial/Liability
• Topographical Map
Post-Closure Plan
Assemble Part B Application
Submit Application
KEY
Ready Before Part B Underway
Fundamental Elements of the Part B Application
Alternate Procedure

FIGURE 1. Preparing a RCRA permit part B application for a land treatment facility.

information which shows the identified hazardous constituents can be transformed, degraded, or immobilized within the treatment zone of the facility.

It is important to note that the objective of land treatment is not to degrade the applied waste to background concentrations. The objective is to degrade the applied waste constituents so that they will not leach out of the treatment zone in the foreseeable future and that the constituents will be transformed to a nontoxic level.

WASTE CHARACTERISTICS

The hazardous constituents which must be evaluated in the treatment demonstration are those identified in Appendix VIII of 40 CFR 261. The Appendix VIII list contains over 350 chemicals and compounds. In order to identify the Appendix VIII constituents which are known or suspected of being present in land treated petroleum wastes, Environmental Research and Technology, Inc. (ERT) conducted a detailed literature review of waste characteristics data (ERT 1984). The review was conducted for the American Petroleum Institute and included data from the following sources: (1) analyses of petroleum refinery wastes which are land treated, (2) analyses of petroleum refinery wastewaters, (3) analyses of soils at petroleum refinery land treatment facilities, (4) analyses of crude oil and refined products, (5) discussions with individuals knowledgeable of petroleum refinery process and waste management operations.

Table 1 shows the constituents identified from the review of waste characteristics data. These constituents can be grouped according to similar physical/chemical characteristics into the following categories: inorganics—metals and cyanide, monoaromatic hydrocarbons, polycyclic aromatic hydrocarbons, phenolics, phthalate esters. Notably absent from Table 1 are chlorinated organic Appendix VIII constituents. These constituents are not expected to be present in petroleum industry wastes as halogenation is not normally a refinery unit operation. The constituents shown in Table 1 provide a valuable screening mechanism reducing the number of samples and analyses required to adequately characterize site specific wastes.

DEGRADATION OF ORGANIC COMPOUNDS

The degradation of most organic compounds in the soil will follow a first-order reaction ($dc/dt = KC$). The reaction indicates that at any one time, the rate of degradation is proportional to the concentration of the compound in the soil. First-order kinetics generally apply where the concentration of the compound being degraded is low relative to the biological activity in the soil (Kaufman et al. 1983). At very high concentrations, Michaelis-Menten Kinetics seem to apply and the rate of decomposition changes from being proportional to the concentration to being independent of concentration (Kaufman et al. 1983).

Degradation times can be estimated from first order rate constants by solving the differential equation:

TABLE 1. Appendix VIII constituents known or suspected to be present in refinery wastes which are land treated.[1]

Known to be Present	Suspected to be Present
Arsenic	Anthracene
Benzene	Antimony
Bis(2-ethylhexyl)phthalate	Barium
butyl benzyl phthalate	Benz(c)acridine
Benz(a)anthracene	Benzo(b)fluoranthrene
Benzo(a)pyrene	Benzo(j)fluoranthrene
Benzo(k)fluoranthrene	Cobalt
Beryllium	Dibenz(a,h)acridine
Cadmium	Dibenz(a,j)acridine
Chromium	Dibenz(a,h)anthracene
Chrysene	Dibenz(c,g)carbazole
Copper[2]	Dibenz(a,e)pyrene
Cyanide	Dibenz(a,h)pyrene
Fluoranthene	Dibenz(a,i)pyrene
Lead	Diethyl phthalate
Mercury	Dimethyl phthalate
Naphthalene	Ethylene dibromide
Nickel	Ethylene dichloride
Phenol	7,12-dimethylbenz(a)anthracene
Selenium	2,4-dimethyl phenol
Toluene	4,6-dinitro-o-cresol
Vanadium	2,6-dinitrotoluene
Zinc[2]	2,4-dinitrophenol
1-methyl naphthalene[2]	di-n-butylphthalate
2-methyl naphthalene[2]	di-n-octylphthalate
Phenanthrene[2]	Hydrogen sulfide
	Indeno(1,2,3-cd)pyrene
	Nitrobenzene
	4-nitrophenol
	P-cresol
	Tetraethyl Lead

---

[1] A list of constituents suspected to be present is currently being developed by EPA as of 5/84.

[2] Non-Appendix VIII constituents.

$$t = \frac{\ln (c_t/c_o)}{-K} \qquad (1)$$

where: c_o = initial concentration of the constituent in soil, c_t = final concentration of the constituent in soil, K = first order rate constant for the constituent.

First order rate constants for the Appendix VIII constituents suspected to be present in petroleum wastes are summarized in Table 2. These rate constants can be used to estimate degradation times at specific land treatment facilities. Care should be taken when using the rate constants in Table 2 for different waste loading conditions. If the constituent is present in the waste at high concentrations, potential toxicity effects to soil microbes should also be considered.

MIGRATION OF ORGANIC COMPOUNDS

The sediment/water partition coefficient (K_p) is often used to describe the partitioning of organic solvents between water and solids in soil solutions. This parameter is widely used in studies of groundwater contamination and can be used to describe the mobility of waste constituents in soil at land treatment systems. The time for a constituent to migrate through soil can be estimated from the following equation (Enfield et al. 1982):

$$t = \frac{z}{V + (1 + (P/\theta)\ Kp)} \qquad \text{(Enfield et al. 1982)} \qquad (2)$$

where: z = depth of soil (cm), V = velocity of water (cm/day), P/n = bulk density of soil/porosity of soil (g/cm^3), K_p = sediment/water partition coefficient (ml/g).

For a given climate, V may be considered as the net recharge (precipitation-evapotranspiration) divided by the porosity (n) of a soil, assuming no runoff.

Table 3 summarizes migration times for different Kp values assuming: V = (10 cm precip. - 5 cm evaporation)/month = 0.8 cm/day; z = 30 cm of soil; P = 1.3 g/cm^3; θ = 0.2.

A soil depth of 30 cm was used for the calculations to illustrate the time for a constituent to migrate below the zone of incorporation. It is apparent from Table 3 that when Kp is greater than 100, migration times are extremely long and the solute is essentially immobile. Much longer migration times would occur if the full depth of the treatment zone were utilized (150 cm).

Sediment/water partition coefficients can be estimated from organic carbon partition coefficients if the organic carbon content of the soil is known.

$$K_p = K_{oc} \times f_{oc} \qquad (3)$$

where: K_{oc} = organic carbon partition coefficient of the Appendix VIII constituent, f_{oc} = fractional mass of organic carbon in the soil.

TABLE 2. Kinetic parameters describing rates of degradation of organic compounds in soil systems.

Substance	Initial Concentration (mg/g soil)	K (day^{-1})	1/2 Life (days)	Reference
Toluene	5,000-20,000	0.40-1.0	0.7-1.7	Overcash et al. 1982
Toluene	–	0.10	7	Berkowitz et al. 1981
Pyridine	–	>0.10	<7	Berkowitz et al. 1981
Phenol	500	0.693	1.0	Medvedev & Davidov 1972
Phenol	500	0.315[1]	2.2[1]	Medvedev & Davidov 1972
2,4-dimethylphenol	500	0.35-0.69	1-2	Medvedev & Davidov 1972
4,6-dinitro-o-cresol	–	>0.023	<30	Versar, Inc. 1979
2,4-dinitrophenol	5-50	0.025	28	Overcash et al. 1982
2,4-dinitrophenol	20-25	>0.099-0.23	<3-7	Sudharkar-Barik & Sethunathan 1978
4-nitrophenol	–	>0.043	<16	Verschueren 1977
Bis(2-ethylhexyl phthalate)	–	0.050	14	Johnson and Lulves 1975
Diethyl Phthalate	10	>0.173	<4	McDuffie & Russell 1982
Napthalene	7	5.78	0.12	Herbes & Schwall 1978
Napthalene	7	0.005[1]	125[1]	Herbes & Schwall 1978
Napthalene	7	0.173	4[2]	Herbes & Schwall 1978
Benz(a)anthracene	0.12	0.046[1]	15.2[1]	Herbes & Schwall 1978
Benz(a)anthracene	0.12	0.0001	6,250	Herbes & Schwall 1978
Benz(a)anthracene	3.5	0.007	102	Groenewegen & Stolp 1976
Benz(a)anthracene	20.8	0.003	231	Gardner et al. 1979

[1] Low temperature (<15°C)

[2] High temperature (>25°C)

TABLE 2. Continued.

Substance	Initial Concentration (mg/g soil)	K (day^{-1})	1/2 Life (days)	Reference
Benz(a)anthracene	25.8	0.005	133	Gardner et al. 1979
Benz(a)anthracene	17.2	0.008	199	Gardner et al. 1979
Benz(a)anthracene	22.1	0.006	118	Gardner et al. 1979
Benz(a)anthracene	42.6	0.003	252	Gardner et al. 1979
Benz(a)anthracene	72.8	0.004	196	Gardner et al. 1979
Benz(a)anthracene	0.07	0.005	134	Sims 1982
Benz(a)anthracene	0.10	0.005	142	Sims 1982
Benz(a)anthracene	0.15	0.005	154	Sims 1982
Benz(a)anthracene	7	0.016	43	Sims 1982
Benz(a)anthracene	8.2	0.017	41	Sims 1982
Benz(a)anthracene	9.7	0.017	41	Sims 1982
Chrysene	4.4	0	–	Sims 1982
Chrysene	500	0.067	10.5	Groenewegen & Stolp 1976
Chrysene	5	0.126	5.5	Medvedev & Davidov 1972
Dibenz(a,j)-acridine	0.57	0.015	44	Medvedev & Davidov 1972
Dibenz(a,j)-acridine	0.71	0.017	40	Sims 1982
Dibenz(a,j)-acridine	0.69	0.012	55	Sims 1982
Dibenz(a,j)-acridine	57	0.016	43	Sims 1982
				Sims 1982

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[1] Low temperature (<15°C)

[2] High temperature (>25°C)

TABLE 2. Continued.

Substance	Initial Concentration (mg/g soil)	K (day^{-1})	1/2 Life (days)	Reference
Dibenz(a,j)-acridine	64	0.017	41	Sims 1982
Dibenz(a,j)-acridine	73	0.015	46	Sims 1982
Indeno(1,2,3-cd)-pyrene	0.57	0.001	600	Sims 1982
Indeno(1,2,3-cd)-pyrene	1.14	0.002	360	Sims 1982
Indeno(1,2,3-cd)-pyrene	1.30	0.003	200	Sims 1982
Indeno(1,2,3-cd)-pyrene	57	0.001	600	Sims 1982
Indeno(1,2,3-cd)-pyrene	114	0.001	600	Sims 1982
Indeno(1,2,3-cd)-pyrene	168	0.001	600	Sims 1982
Dibenz(a,h)-anthracene	9700	0.033[2]	21[2]	Lijinsky & Quastel (1956)
Dibenz(a,h)-anthracene	5.7	0.004	183	Sims 1982
Dibenz(a,h)-anthracene	4.5	0.005	141	Sims 1982
Dibenz(a,h)-anthracene	3.5	0.004	190	Sims 1982
Dibenz(a,h)-anthracene	57	0.005	130	Sims 1982
Dibenz(a,h)-anthracene	93	0.007	99	Sims 1982
Dibenz(a,h)-anthracene	147	0.007	119	Sims 1982
Fluoranthene	3.9	0.016	44	Groenewegen & Stolp 1976
Fluoranthene	18.0	0.004	182	Gardner et al. 1979
Fluoranthene	23.0	0.007	105	Groenewegen & Stolp 1976
Fluoranthene	16.5	0.005	143	Gardner et al. 1979

[1] Low temperature (<15°C)

[2] High temperature (>25°C)

TABLE 2. Continued.

Substance	Initial Concentration (mg/g soil)	K (day^{-1})	1/2 Life (days)	Reference
Fluoranthene	20.9	0.006	109	Groenewegen & Stolp 1976
Fluoranthene	44.5	0.004	175	Gardner et al. 1979
Fluoranthene	72.8	0.005	133	Gardner et al. 1979
Benzo(b)fluoranthene	0.33	0.007	98	Sims 1982
Benzo(b)fluoranthene	0.57	0.006	123	Sims 1982
Benzo(b)fluoranthene	0.80	0.006	130	Sims 1982
Benzo(b)fluoranthene	33	0.010	67	Sims 1982
Benzo(b)fluoranthene	46	0.008	85	Sims 1982
Benzo(b)fluoranthene	53	0.010	73	Sims 1982
Benz(a)pyrene	0.048	0.014[1]	50[1]	Herbes & Schwall 1978
Benz(a)pyrene	0.01	0.001[1]	694[1]	Herbes & Schwall 1978
Benz(a)pyrene	3.4	0.012	57	Groenewegen & Stolp 1978
Benz(a)pyrene	9.5	0.002	294	Gardner et al. 1979
Benz(a)pyrene	12.3	0.005	147	Gardner et al. 1979
Benz(a)pyrene	7.6	0.003	264	Gardner et al. 1979
Benz(a)pyrene	18.5	0.023	30	Gardner et al. 1979
Benz(a)pyrene	17.0	0.002	420	Gardner et al. 1979
Benz(a)pyrene	32.6	0.004	175	Gardner et al. 1979

---

[1] Low temperature (<15°C)

[2] High temperature (>25°C)

TABLE 2. Continued.

Substance	Initial Concentration (mg/g soil)	K (day^{-1})	1/2 Life (days)	Reference
Benz(a)pyrene	1.0	0.347[2]	2[2]	Shabad et al. 1975
Benz(a)pyrene	0.515	0.347[2]	2[2]	Shabad et al. 1975
Benz(a)pyrene	0.00135	0.139[2]	5[2]	Shabad et al. 1975
Benz(a)pyrene	0.0094	0.002[1]	406[1]	Shabad et al. 1975
Benz(a)pyrene	0.545	0.011	66	Shabad et al. 1975
Benz(a)pyrene	28.5	0.019[1]	37[1]	Shabad et al. 1975
Benz(a)pyrene	29.2	0	–	Shabad et al. 1975
Benz(a)pyrene	9,100	0.018[2]	39[2]	Liginsky & Quastel 1956
Benz(a)pyrene	19.5	0.099	7	Poglazova et al. 1967
Benz(a)pyrene	19.5	0.139	5	Poglazova et al. 1967
Benz(a)pyrene	19.5	0.231	3	Poglazova et al. 1967
Benz(a)pyrene	130.6	0.173	4	Poglazova et al. 1967
Benz(a)pyrene	130.6	0.116	6	Poglazova et al. 1967
Benz(a)pyrene	0.36	0.009	79	Sims 1982
Benz(a)pyrene	0.41	0.008	83	Sims 1982
Benz(a)pyrene	0.75	0.006	120	Sims 1982
Benz(a)pyrene	36	0.008	92	Sims 1982
Benz(a)pyrene	55	0.007	100	Sims 1982
Benz(a)pyrene	69	0.008	92	Sims 1982

[1] Low temperature (<15°C)

[2] High temperature (>25°C)

TABLE 3. Migration time[1] for constituents based on partition coefficients.

Kp ml/g	Z (cm)	V (cm/day)	P/n gm/cm^3	t (days)	t (years)
0.1	30	0.8	6.5	61	0.17
1.0	30	0.8	6.5	281	0.77
10	30	0.8	6.5	2475	6.78
100	30	0.8	6.5	24,412	66.9
1,000	30	0.8	6.5	243,787	668.
10,000	30	0.8	6.5	2,437,537	6680.

[1] To migrate through 30 cm of soil.

This relationship has been shown to be valid for hydrophobic adsorption (Karickhoff et al. 1979, Mean et al. 1979). The equation generally underestimates soil sorption of more soluble, less hydrophobic compounds. The K_{oc} value for a constituent is independent of soil properties and is a unique property of the compound being solved. Thus, if K_{oc} has been determined for a hydrophobic constituent, sediment water partition coefficients (K_p) can be estimated for a variety of soils if the organic carbon content of each soil is known.

Hydrophobic sorption has been shown to be highly correlated with the partitioning of the compounds between octanol and water. Figure 2 shows the relationship between K_{oc} and octanol/water partition coefficients for several petroleum related compounds. The regression equation in Figure 2 allows prediction of a K_{oc} value for a hydrophobic compound if the K_{ow} for the compound is known. A similar but inverse relationship was also reported between K_{oc} and water solubilities. However, this relationship was less reliable because of the difficulty in obtaining good solubility data for highly hydrophobic compounds.

Table 4 summarizes K_{oc} data for the Appendix VIII organics present in petroleum industry wastes. Octanol/water partition coefficients (K_{ow}) and water solubility data are also provided. Site specific sediment water partition coefficients (K_p can be estimated from K_{oc} and K_{ow} data using the relationships provided. For those constituents for which there are no measured K_{oc} and K_{ow} values, sediment water partition coefficients can be estimated from adsorption data for compounds with similar physical and chemical characteristics.

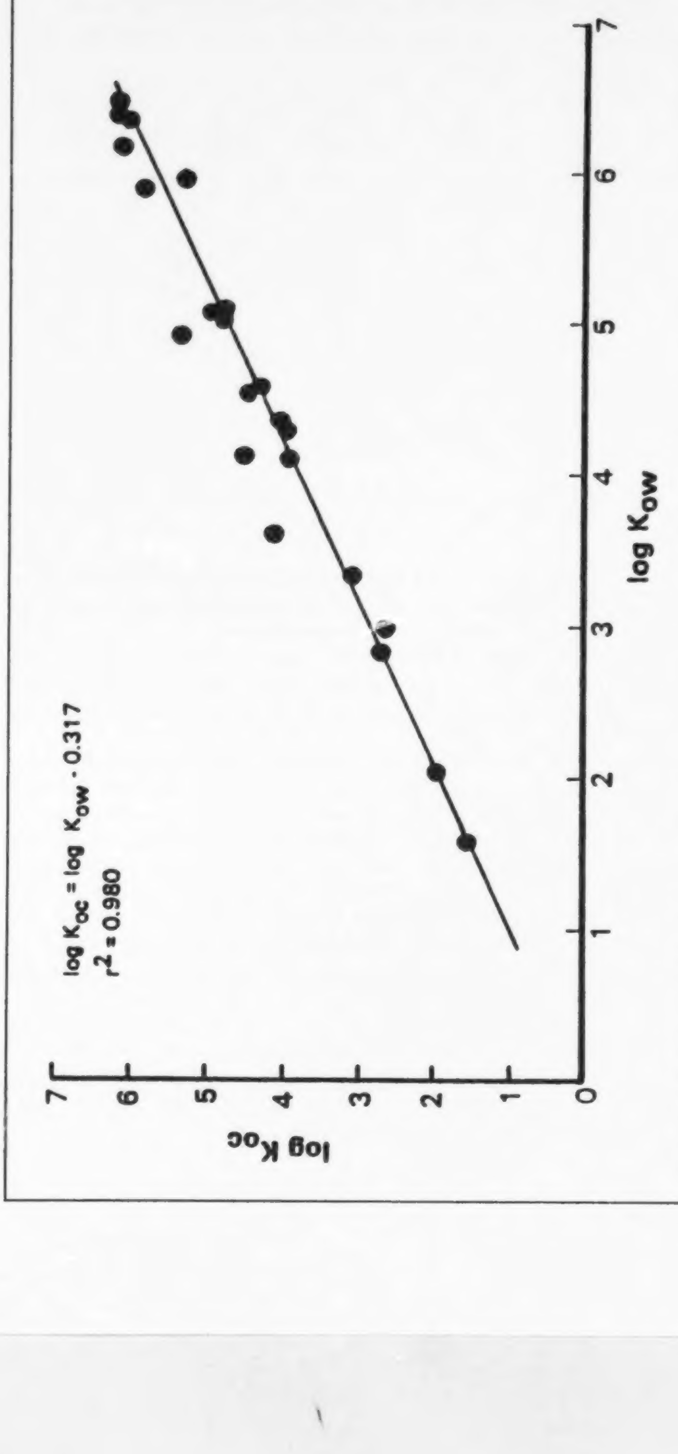

FIGURE 2. Relationship between K_{OC} and octanol-water partition coefficient (K_{OW}) of petroleum related organic compounds (Hassett et al. 1980).

TABLE 4. Summary of soil adsorption data for organic constituents.

Compound	Aqueous Solubility (mg/l)	log octanol/ water parti- Coefficient Kow	Organic Carbon Partition Coefficient Koc
Monoaromatics			
Benzene	1780-1800 (25C)	1.95-2.13	83[1]
Toluene	535 (25C)	2.69	No Data
Nitrobenzene	1000 (20C)	1.85	No Data
2,4-Dinitrotoluene	270 (22C)	2.01	No Data
2,6-Dinitrotoluene	No Data	2.05	No Data
Phenolics			
Phenol	93,000 (25C)	1.46	2,900[6]
2,4-Dimethylphenol	4,200 (20C)	2.50	No Data
4,6-Dinitro-o-cresol		2.85	No Data
4-Nitrophenol	16,000 (25C)	1.91	No Data
2,4-Dinitrophenol	5,600 (18C)	1.53	No Data
Phthalate Esters			
Bis (2-ethylhexyl)	0.4 (25C)	5.3-8.7	31,700[2]
Butyl Benzyl	2.9	4.8-5.8	21,900[2]
Diethyl	896 (25C)	3.22	1,870[2]
Di-n-octyl	3.0 (25C)	9.2	No Data
Dimethyl	4320 (25C)	2.12	No Data
Polynuclear Aromatic Hydrocarbons			
Benz(c)acridine	No Data	No Data	No Data
Benz(a)Anthracene	0.014	5.61	1,871,400[3]
Benzo(b)Fluoranthene	0.0012	6.57	No Data
Benzo(j)Fluoroanthene	No Data	No Data	No Data
Benzo(a)Pyrene	0.005	6.04	4,510,640[4]
Chrysene	0.0018	5.61	No Data
Dibenz(a,h)Acridine	No Data	No Data	No Data
Dibenz(a,j)Acridine	No Data	No Data	No Data
Dibenz(a,h)Anthracene	0.005	5.97	2,029,000[5]
7H Dibenzo(c-g)-Carbazole	No Data	No Data	No Data
Dibenzo(a,e)Pyrene	No Data	No Data	No Data
Dibenzo(a,h)Pyrene	No Data	No Data	No Data
Dibenzo(a,i)Pyrene	No Data	No Data	No Data
7,12-Dimethylbenz(a)-Anthracene	0.244	5.97	225,308[5]
Fluoranthene	0.26	5.33	No Data
Indeno(1,2,3-cd)-Pyrene	0.0002	7.66	No Data
Naphthalene	31.7	3.37	1,300[4]

[1] Karickhoff et al. 1979

[2] McDuffie and Russell 1982

[3] Hasset et al. 1980

[4] Reinbold et al. 1978

[5] Means et al. 1979

[6] Isaascon and Frink 1984

TREATMENT EVALUATIONS

The principal concern involved in the land treatment of petroleum wastes is the potential for the hazardous constituents in the waste to leach beyond the treatment zone of the facility. Extensive data from petroleum industry land treatment sites (ERT 1983, Canviro Consultants 1983) indicate that the Appendix VIII inorganics are effectively immobilized in the soil provided appropriate management practices are followed. Therefore, most of the effort involved in preparing a treatment demonstration will be expended evaluating the treatability of the organic Appendix VIII constituents. The reader is referred to the above reports if additional information is needed concerning the treatability of Appendix VIII inorganics.

Figure 3 presents a methodology for evaluating the migration potential of organic compounds. The methodology is a first-level screening which identifies those constituents which may migrate beyond the treatment zone and should be subject to additional evaluation. Wastes, site and operational factors are the input data to the screening model. Using known or estimated organic carbon partition coefficients, a site specific partition coefficient (Kp) can be estimated for the constituent being evaluated.

If K_p is greater than 100, then the constituent is essentially immobile and no further evaluation is necessary. If K_p is less than 100, then the migration time (t_m) and the degradation time (t_d) are compared. Migration and degradation times can be estimated using rate constants which describe the sorption and degradation of organic compounds in soil. Degradation and adsorption rate constants and equations for estimating degradation and migration times were presented in the earlier sections.

If t_d is less than t_m, then the compound will degrade before it moves beyond the treatment zone and no further evaluation is necessary. If t_d is greater than t_m, the evaluator may select to evaluate the degradation and adsorption rate constants extrapolated from the literature and develop site specific rate constants. These constants could be developed through laboratory and pilot studies or by selecting the compound as a PHC in a long-term monitoring program. In most cases the treatment demonstration will need to be prepared in two steps. First, a literature demonstration using available literature and existing monitoring data should be conducted. Next, a field demonstration should be carried out to monitor the fate of the constituents identified in the literature demonstration as difficult to treat.

TREATMENT DEMONSTRATION—EXAMPLE

In this example, the time to degrade different Appendix VIII organics is compared to the time for these compounds to migrate out of the incorporation zone of a petroleum refinery land treatment facility. The refinery applies a mixed waste consisting of API separator sludge, slop oil emulsion solids, crude tank bottoms, and wastewater treatment sludge to a 40-acre land treatment site in the Gulf Coast region. Waste concentrations of the Appendix VIII organic constituents are shown in Table 5. Soil and operational data for the facility are shown in Table 6.

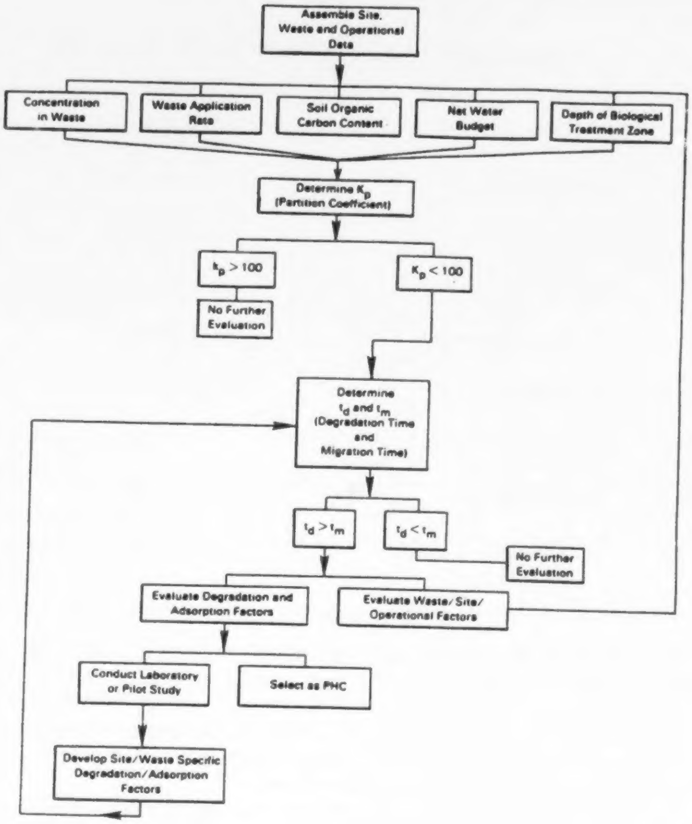
Assemble Site, Waste and Operational Data
Concentration in Waste
Waste Application Rate
Soil Organic Carbon Content
Net Water Budget
Depth of Biological Treatment Zone
Determine K_p (Partition Coefficient)
$K_p > 100$
$K_p < 100$
No Further Evaluation
Determine t_d and t_m (Degradation Time and Migration Time)
$t_d > t_m$
$t_d < t_m$
No Further Evaluation
Evaluate Degradation and Adsorption Factors
Evaluate Waste/Site/Operational Factors
Conduct Laboratory or Pilot Study
Select as PHC
Develop Site/Waste Specific Degradation/Adsorption Factors

FIGURE 3. Methodology for determining migration potential of selected Appendix VIII organics.

TABLE 5. Waste characteristics for gulf coast refinery.

Constituent	Concentration (ppm)
Naphthalene	1,000-10,000
Nitrobenzene	100-1,000
Benzene	100-1,000
Toluene	100-1,000
2,4-dimethyl phenol	10-100
Fluoranthene	10-100
Benzo(a)anthracene	1-10
Benzo(a)pyrene	1-10
Chrysene	1-10

The data shown in Tables 5 and 6 are used as input to the screening model. Table 7 summarizes the results of the model and compares the time for the organic constituents to migrate 30 cm with the time estimated for these compounds to degrade below detection limits ($C_t \sim 0.10$ ppm). Degradation times were estimating from first order rate constants using equation (1). Migration times were estimated from K_{oc} data using equations (2) and (3).

For conservative estimating purposes, the velocity of water passing through the soil was estimated using data for the wettest month of the year:

$$V = \frac{\text{net recharge in February}}{\text{soil porosity}} = \frac{2.13 \text{ cm/month}}{30 \text{ days/month}} \div 0.30 = 0.24 \text{ cm/day}$$

Degradation times were also conservatively estimated using the highest reported waste constituent concentrations. Table 7 clearly shows that compounds with K_p values greater than 100 are immobilized within the zone of incorporation. Compounds with K_p values less than 100 are degraded before they migrate less than 30 cm.

The ratio of the migration time (t_m) to the degradation time (t_d) for each constituent is also included in Table 7. This ratio can be used to indicate the relative factor of safety in the theoretical calculations. Even using worst case conditions

TABLE 6. Site characteristics for gulf coast refinery.

Parameter	
Land treatment area	40 acres
Waste loading rate	500,000 lb/acre-year
Depth of incorporation zone	12 inches
Depth of treatment zone	60 inches
Soil porosity (n)	0.30
Soil bulk density (p)	1.5 g/cm^3
Soil organic carbon content (f_{oc})	0.011
Monthly Water Balance	P-ET
January	1.83 cm
February	2.13 cm
March	-2.46 cm
April	-3.96 cm
May	-5.85 cm
June	-10.32 cm
July	-13.82 cm
August	-9.87 cm
September	-2.00 cm
October	-1.98 cm
November	-0.45 cm
December	1.10 cm

(high waste concentrations, low degradation rates, high recharge) the degradation times were less than the migration times for each constituent. Under more normal conditions, differences between degradation times and migration times would increase further.

The ratio between migration and degradation times can be used to select constituents for field treatabilty studies. Similarly, those constituents with the lowest ratios are the most difficult to treat and therefore most suitable as PHCs in an unsaturated zone monitoring program. For the example, benzene 2,4-dimethyl phenol, nitrobenzene, and napthalene have the lowest ratios and are therefore most difficult to treat. These constituents would therefore be best suited for field treatability studies.

SUMMARY

Available literature data can be used to estimate soil adsorption capacities and degradation rates for Appendix VIII organics present in petroleum industry wastes. A methodology is presented in this paper which incorporates these data

TABLE 7. Comparison of migration times with degradation times for Appendix VIII organics.

Compound	Concentration[1] in Waste (ug/g)	Concentration[2] in Soil (ug/g)	First Order Rate[3] Constant, K (day^{-1})	Partition[4] Coefficient, Kp (ml/g)	Degradation[5] Time (days)	Migration[6] Time (days)	T_m/T_D
Naphthalene	10,000-10,000	125.-1,250	0.01-0.1	14.3	94-940	9,000	9.5
Nitrobenzene	100-1,000	12.5-125	0.1-1.0	0.37	7-70	360	5.1
Benzene	100-1,000	12.5-125	0.1-1.0	0.90	7-70	690	9.8
Toluene	100-1,000	12.5-125	0.1-1.0	2.60	7-70	1,750	25
2,4-dimethyl phenol	10-100	1.25-12.5	0.01-0.1	3.7	48-480	2,400	5
Fluoranthene	10-100	1.25-12.5	0.001-0.01	1,100	480-4,800	650,000	135
Chrysene	1-10	0.125-1.25	0.001-0.01	2,200	250-2,500	1,300,000	520
Benz(a)anthracene	1-10	0.125-125	0.001-0.01	2,200	250-2,500	1,300,000	520
Benz(a)pyrene	1-10	0.125-1.25	0.001-0.01	50,000	250-2,500	6,000,000	2,400

[1] Source: Table 5.

[2] Concentration in the soil immediately after waste application assuming 1 annual waste application, a waste loading rate of 500,000 lb/acre-yr, a depth of incorporation of 12 inches, and a soil bulk density of 1.5 g/cm^3.

[3] Source: Estimated from Table 2.

[4] Source: Estimated from Table 4.

[5] Time for a compound to degrade to a soil concentration of 0.10 ug/g (for highest waste concentration).

[6] Time for a compound to migrate 30 centimenters (12 inches).

with site and waste specific factors to evaluate the relative treatability of any given waste at any given site. The methodology quickly screens a wide group of Appendix VIII compounds and eliminates the need for extensive laboratory or field studies. The methodology identifies those constituents present in the waste that are the most difficult to treat and require additional evaluation in field studies or an unsaturated zone monitoring program. It should be noted that the data base for degradation and adsorption constants in a complex matrix is currently limited. As this data base is expanded the need for costly and extensive field studies can be minimized through the use of the proposed screening methodology.

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APPENDIX A
SYSTEM INTERNATIONAL AND OTHER CONVERSIONS USED IN THIS BOOK

To Convert From:	Multiply by:	To Obtain:	Units:
Area			
acre	x 4 047	= meter^2	m^2
foot^2	x 0.092 90	= meter^2	m^2
hectare	x 1.000 E-4	= meter^2	m^2
inch^2	x 6.452 E-4	= meter^2	m^2
mile^2	x 2.590 E-6	= meter^2	m^2
yard^2	x 0.836 1	= meter^2	m^2
Energy or Work			
BTU	x 1 055	= joule	J
Length			
inch	x 2.54	= centimeter	cm
foot	x 0.304 8	= meter	m
inch	x 0.025 40	= meter	m
mile, nautical	x 1 852	= meter	m
mile	x 1 609	= meter	m
yard	x 0.914 4	= meter	m
Mass			
ounce$_{mass}$(avoird.)	x 0.028 3	= kilogram	kg
pound$_{mass}$(avoird.)	x 0.453 6	= kilogram	kg
ton (long, 2240 lb$_m$)	x 1 016	= kilogram	kg
ton (short, 2000 lb$_m$)	x 907.2	= kilogram	kg
ton (metric)	x 1 000	= kilogram	kg
Volume or Capacity			
acre-foot	x 1 233	= meter^3	m^3
foot^3	x 0.028 32	= meter^3	m^3
gallon (U.S. liquid)	x 0.003 785	= meter^3	m^3
inch^3	x 1.639 E-5	= meter^3	m^3
liter	x 0.001 000	= meter^3	m^3
yard^3	x 0.764 6	= meter^3	m^3
Volume/Time or Discharge or Flow Rate			
foot^3/second	x 0.028 32	= meter^3/second	m^3/s
foot^3/minute	x 4.719 E-4	= meter^3/second	m^3/s
gallon/minute	x 6.309 E-5	= meter^3/second	m^3/s
gallon/day	x 4.381 E-8	= meter^3/second	m^3/s

Temperature

$C^\circ = (F^\circ - 32)\ 5/9$

$F^\circ = C^\circ\ 9/5 + 32$

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